## Introduction to a Theory of Ortho-Para H<sub>2</sub> Conversion on Paramagnetic Catalysts: The Magnetic Field Effect

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The application of an external magnetic field, during the conversion of  $o-H_2$  into  $p-H_2$ , mixes the catalyst paramagnetic impurity wave functions, opening, therefore, new o-ptransitions of different symmetry. The dynamical polarization of either the surface electronic spins or the H<sub>2</sub> nuclear spins, induced by the H<sub>2</sub> rotational system, strongly enhances the catalytic rates.

Ortho-para hydrogen conversion has been one of the first catalytic reactions to receive a physical and theoretical interpretation, in 1933.<sup>1</sup> Since then, Wigner's theory, derived in the homogeneous case, has been applied by all authors, in heterogeneous conversion as well. A first failure of this theory when applied to ferromagnetic catalysts has already been reported.<sup>2</sup> Now, during the past ten years, Selwood has reported numerous experimental results, dealing with large alterations of the conversion rates, when applying an external magnetic field.<sup>3</sup> Interpretation of these effects leads us to conclude a new failure of Wigner's theory, when applied to paramagnetic catalysts.

In the following, unless otherwise specified, we are dealing with chromia impurities dispersed on an alumina support and at room temperature.<sup>4</sup> The various processes considered are shown in Fig. 1. After being prepared in a definite proportion of ortho and para states far different from the equilibrium value, hydrogen molecules collide with the surface catalyst in a continuous flow. It is known that, for an  $H_2$  molecule, if I(L) denotes its nuclear (rotational) angular momentum, because of Pauli's principle, the ortho (para) states correspond to odd (even) values of I and L. At the surface, the (2L+1)-fold rotational degeneracy is removed by the interaction of the surface electric-field gradients with the quadrupolar moment Q of the H<sub>2</sub> nuclei. If we assume an axially symmetric potential V (around an axis OZ) the rotational Hamiltonian for the molecule is simply

$$M = \frac{L^2}{2g} + \frac{eQ}{8} \frac{\partial^2 V}{\partial Z^2} (3\cos^2\theta - 1),$$

where  $\theta$  is the usual polar angle and  $\mathcal{G}$  the H<sub>2</sub> moment of inertia. If necessary M may also include the  $\mathbf{I} \cdot \mathbf{L}$  interaction, the Zeeman term as well as the intermolecular interaction. The magnetic impurity spin states may be described by a "spin-Hamiltonian" formalism. Here it takes the simple form

$$S = -Ds_{\xi}^{2} + g\mu_{B}\overline{H}_{0} \cdot \overline{S} \quad (s = \frac{3}{2}),$$

where s is the impurity electronic spin momentum. The first term, arising from spin-orbit coupling, holds for the magnetocrystalline anisotropy, whose amplitude is D, the direction  $O\xi$  and the symmetry trigonal. The second one is the Zeeman term. For concentrated samples S may include dipolar and exchange interactions with neighbors. Thermal averages will be done on an ensemble of classical variables, describing the exchange of molecules between the adsorbed phase and the hydrogen flow, the rotational and translational diffusion of the adsorbed molecules, the phonons which ensure the thermal contact between the spins  $\overline{s}$  and the thermostat at temperature T. The "thermodynamical system" is open since molecules are continually renewed.  $\Re_{0}$ =M + S constitutes the unperturbed Hamiltonian with respect to the dipolar interactions which couple each impurity spin  $\overline{s}$  with the two proton nuclear spins  $\overline{I}_1, \overline{I}_2$  and the rotational momentum L of each adsorbed molecule, considered as a



FIG. 1. Illustration of the different processes, and their characteristic times, involved in o-p hydrogen conversion on paramagnetic catalysts.

small perturbation of Hamiltonian  $\mathcal{K}_1$ . Dividing it, as usual, into symmetrical  $\mathcal{K}_1^{S}$  and antisymmetrical  $\mathcal{K}_1^{AS}$  parts, under interchange of the two protons, we have

$$\mathcal{K}_{1} = \mathcal{K}_{1}^{AS} + \mathcal{K}_{1}^{S},$$

$$\mathcal{K}_{1}^{AS} = \vec{s} \cdot \vec{D}_{1}(\vec{r}, \theta, \varphi) \cdot [\vec{I}_{1} - \vec{I}_{2}],$$

$$\mathcal{K}_{1}^{S} = \vec{s} \cdot \vec{D}_{2}(\vec{r}, \theta, \varphi) \cdot [\vec{I}_{1} + \vec{I}_{2}] + \vec{s} \cdot \vec{D}_{2}(\vec{r}) \cdot \vec{L}.$$
(1)

where the polar angles  $(\theta, \varphi)$  refer to the molecule rotation. The detailed expansion of  $\overline{D}_1$  may be found in Petzinger and Scalapino<sup>5</sup>; the extension to  $\overline{D}_2$ , although of different symmetry, and  $D_3$  is straightforward. In this "semi"-classical formalism, the thermal influence is described by the time dependence of the relative position of the center of mass of a molecule  $\mathbf{r}(t)$ . At high temperatures, for instance, the surface layer hydrogen motion may be represented by a twodimensional diffusion equation. The first part of (1),  $\mathfrak{K}_1^{AS}$ , commutes neither with  $L^2$  nor with  $I^2$ , and therefore induces ortho-para H<sub>2</sub> conversions (o-p) which are high-energy transitions ( $\Delta L$  and  $\Delta I = \pm 1$ , of frequencies  $\omega_{op} \approx 10^2$  cm<sup>-1</sup>). In contradistinction,  $\mathfrak{K}_1^{S}$  commutes with  $L^2$  and  $I^2$ , only affects ortho states, and therefore induces less energetic transitions between the nuclear, electronic, and rotational sublevels  $(\Delta m_I, \Delta m_s, \text{ or }$ 

 $\Delta m_L = \pm 1$ , of frequencies  $\omega_I$ ,  $\omega_S$ ,  $\omega_L$  varying from 10<sup>-3</sup> to 10 cm<sup>-1</sup>).

Let us first focus our attention on the conversion interaction  $\mathcal{K}_1^{AS}$  which has a short range, of radius  $\approx 3 \text{ Å}$ ,<sup>5,6</sup> and is thus restricted to the couples of molecule and surface impurity in a narrow vicinity. The time spent by a molecule in that radius ( $\approx 10^{-11} - 10^{-12}$  s) is very short compared to the characteristic time of conversion ( $\tau_{ab}$  $\approx 10^{-3}$  s) and the conversion rate is given by  $(d\langle L^2 \rangle/dt)/L(L+1)$  where the o-p concentration remains close to its initial value (initial slope). As we need to express it in terms of nuclear and rotational operators separately, we remain in the uncoupled representation. The conversion rate, v, is now calculated using a time-dependent perturbation formalism by means of a double commutator. In order to make clear the rate field dependence,  $v(H_0)$ , I introduce the following simplifying (but unessential for this purpose) assumptions: (1) a statistical independence between  $\mathbf{\tilde{s}}$ ,  $\vec{I}_1 - \vec{I}_2$ , and  $\vec{L}$ ; (2) a unique stationary correlation function  $g(\tau)$  describing the time dependence of  $\mathfrak{K}_1^{AS}$  leading to a spectral density  $\mathfrak{G}(\omega_{ab}) = \int_{-\infty}^{+\infty} \mathfrak{K}(\tau)$  $\times \exp(-i\omega_{op}\tau)d\tau$  which represents the thermal energy available at the conversion frequency  $\omega_{op}$ ; (3)  $Oz \parallel \vec{H}_0$  and  $\vec{D} (\parallel 0\xi)$  in the Ozx plane; (4) at moderately low fields,  $H_0 \ll D$ , S eigenfunctions are expressed by a first-order perturbation theory in  $H_0/D$ . Then, a straightforward calculation leads to the following power expansion:

$$v(H_{0}) = J(\omega_{op}) \left\{ \xi \langle L^{2} \rangle + \xi' \langle L_{z}^{2} \rangle + \xi'' \right\} \left\{ \left[ (a \langle s^{2} \rangle + b \langle s_{z}^{2} \rangle) (s \langle I^{2} \rangle + s \langle I_{z}^{2} \rangle) + \langle I_{z} \rangle (e \langle s_{z} \rangle + d \langle s_{z} \rangle) \right] + \frac{H_{0}}{D} \left[ \langle I_{z} \rangle (e \langle s^{2} \rangle + f \langle s_{z}^{2} \rangle) + (g \langle s_{z} \rangle + h \langle s_{z} \rangle) (t \langle I^{2} \rangle + u \langle I_{z}^{2} \rangle) \right] \right\} \circ \{ \text{eq.} \}.$$

$$(2)$$

The factors  $\xi, \ldots, u$  are known angular functions,  $\langle \rangle$  indicates a double quantum and statistical average, and {eq.} corresponds to an equilibrium average of the same expression. At high fields,  $H_0 \gg D$ , S eigenfunctions become independent of  $H_0$ , and so does  $v(H_0)$ . We thus obtain the same qualitative behavior for the field acceleration  $\gamma(H_0) = [v(H_0) - v(0)]/v(0)$  as Selwood, namely, a linear dependence at low fields and a saturation value at high fields. The turning point where  $\gamma$ changes its behavior could be used as a measure of the surface anisotropy D. For a dilute sample it is found that  $D \approx 2500$  G, close to the usual bulk value. Moreover, I remark that v(0) is composed of even powers of operator components, whereas  $v(H_0) - v(0)$  contains odd ones. This is not surprising since v must remain unchanged by a si-

multaneous reversal of the frame of reference and  $H_0$ . The axial symmetry of  $H_0$  has an important consequence: To first order the acceleration  $\gamma$  is linear in the electronic and nuclear magnetizations  $\langle s_{z} \rangle$ ,  $\langle s_{x} \rangle$ , and  $\langle I_{z} \rangle$ . The assumption of Boltzmann distributions would lead to values of  $\gamma$  around  $10^{-2}-10^{-3}$ , in contradiction with experimental results which give 0.2-0.8. Consequently, Selwood's experiments show that in ortho-para H<sub>2</sub> conversion, for a wide scale of temperature and catalysts, there is a strong effect which maintains at least one of these mean values far from equilibrium.

In order to understand this essential point, it is necessary to return to the dipolar part of the interaction,  $\mathcal{R}_1^{S}$ .  $\mathcal{R}_1^{S}$  has a longer range (radius  $\approx 10$  Å) than  $\mathcal{K}_1^{AS}$  and therefore couples each surface spin to more adsorbed molecules, and each molecule to more surface spins (up to the third surface layer). The time spent by a molecule in that "dipolar" radius is longer ( $\approx 10^{-10} - 10^{-11}$  s) than in the "conversion" one. Using the same formalism as before, we introduce the spectral densities  $J(\omega_p)$  where  $\omega_p = \omega_L$ ,  $\omega_s$ , or  $\omega_I$  (or any combination). As  $\omega_{op} \gg \omega_p$ ,  $J(\omega_p) \gg J(\omega_{op})$  and thus the rotational, nuclear, and electronic states are more strongly coupled by the dipolar interaction than by the conversion one. I shall neglect in the following the influence of  $\mathcal{K}_1^{AS}$  and assume a constant ortho molecular concentration close to the initial one. Moreover, at relatively high temperature we have  $\omega_{b} \tau_{d} \ll 1$ ,  $\tau_{d}$  being the translation  $H_2$  diffusion time. I thus define a unique dipolar time  $\tau_{IS} = J^{-1}(\omega_p)$ ,  $(\tau_{IS} \approx 10^{-6} - 10^{-9} \text{ s})$ . Let us now consider the three sets of operator mean values  $\sigma_{\lambda} = \{ \langle s_{z}^{2} \rangle, \langle s_{z} \rangle, \langle s_{x} \rangle \}, \ i_{\mu} = \{ \langle I^{2} \rangle, \langle I_{z}^{2} \rangle, \langle I_{z} \rangle \}, \text{ and } l_{\nu}$ = { $\langle L_{s}^{2} \rangle$ ,  $\langle L_{s} \rangle$ } which appear in Eq. (2). The time evolution of each set is due to the dipolar interactions  $\mathcal{K}_1^{s}$  and to its own relaxation process. For  $\sigma_{\lambda},$  the relaxation is induced by phonon scattering through spin-orbit interaction. If  $\tau_R$  denotes its unique relaxation time, the kinetic equations take the following form:

$$\frac{d\sigma_{\alpha}}{dt} = -\frac{\sigma_{\alpha} - \sigma_{\alpha}^{e}}{\tau_{R}} + \frac{1}{\tau_{IS}} \sum_{\lambda\mu\nu} P_{\lambda\mu\nu} \{\sigma_{\lambda} i_{\mu} l_{\nu} - \sigma_{\lambda}^{e} i_{\mu}^{e} l_{\nu}^{e}\}, \quad (3)$$

where  $P_{\lambda\mu\nu}$  are known angular functions and the superscript e designates an equilibrium average. We may write similar equations for  $i_{\mu}$  and  $l_{\nu}$  [referred in the following as (4) and (5)]. The slow nuclear relaxation ( $\approx 10^{-3}$  s) may be neglected, and the orbital relaxation time, arising either from intermolecular interactions or from phonons, will be denoted by  $au_{OR}$ . As the detailed study of the nonlinear and coupled differential Eqs. (3)-(5) is rather complex, I restrict myself now to some essential qualitative features. I investigate first the case (a)  $\tau_{OR} \ll \tau_{IS} \ll \tau_R$ , corresponding approximately to the experiments performed with the 0.17% Cr<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> catalyst at room "temperature." In this case, molecular reorientation is the faster process and provides a more effective relaxation for the electronic and nuclear spins than their own one. Moreover, molecular reorientation is unable to convert  $o-H_2$  into  $p-H_2$  and therefore leads to a Boltzmann distribution among the rotational ortho states which

differs from the equilibrium one by the ratio  $o_i$  /  $o_e$ ,  $o_i$  and  $o_e$  being the initial and equilibrium orthe concentrations. If now we replace  $l_{y}$  by its steady-state value in (3) and neglect the relaxation term, because  $\tau_{IS} \ll \tau_R$ , we obtain highly polarized steady states for the nuclear and electronic magnetizations. These are roughly of the order of  $(o_i - o_e)$  instead of  $\mu H/kT$  at equilibrium, corresponding to a magnetization enhancement of one to three orders of magnitude. In the case of the plane rotator (with high rotational "barriers"), at low field, when  $O \xi \parallel O Z \perp O z$  the solution of (3) and (4) is straightforward and corresponds to a maximum of polarization:  $\langle s_{g} \rangle = \frac{3}{2}, \langle s_{g}^{2} \rangle = \frac{9}{4}, \langle I_{g} \rangle$  $=\langle I_{s}^{2}\rangle = 1$ . This effect is quite similar to the one encountered in dynamical polarization, as experimented for instance by Solomon.<sup>7</sup> The crossing of a molecule over a surface impurity produces an electric pulse equivalent to the hyperfrequency one applied by Solomon. It induces an energy transfer from the  $H_2$  rotational system to the spin system, through the dipolar coupling term, which corresponds to a thermal mixing between the two systems. (b) When  $\tau_{R} \ll \tau_{IS}$ ,  $\tau_{OR}$  the effect is quite similar to the preceding one. The spin relaxation equalizes the electronic populations as would a hyperfrequency saturating field, inducing strong polarizations of the molecules. Because of the angular form factors and the kinetic constants, these polarizations are differently shared between the nuclear and rotational states. In particular, when  $\tau_{IS} \gg \tau_{OR}$ , the polarization is entirely nuclear. At low temperature, since molecules are more strongly adsorbed, low impurity concentration is sufficient to produce the effect. This seems to be the case observed for 0.17% and 0.0028% Cr<sub>s</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> catalysts at - 100°C. At high temperature, concentrated samples are necessary, which seems to correspond to selfsupported rare-earth catalysts (high-field effect). The o-p H<sub>2</sub> conversion field effects, observed by Selwood, illustrate thus a general result of "thermodynamics of irreversible processes" where dissipative processes may lead to an increase of organization.8,9

Finally, EPR and perhaps NMR experiments, as performed in "CIDNP" effects for instance,<sup>10</sup> would be highly suggestive.

<sup>&</sup>lt;sup>1</sup>E. P. Wigner, Z. Phys. Chem. (Leipzig) <u>B23</u>, 28 (1933).

<sup>&</sup>lt;sup>2</sup>E. Ilisca, Phys. Rev. Lett. <u>24</u>, 797 (1970).

<sup>3</sup>P. W. Selwood, J. Catal. <u>50</u>, 15 (1977), and references therein.

<sup>4</sup>M. Misono and P. W. Selwood, J. Am. Chem. Soc. 91, 1300 (1969).

<u>91</u>, 1300 (1969). <sup>5</sup>K. G. Petzinger and D. J. Scalapino, Phys. Rev. B <u>8</u>, 266 (1973).

<sup>6</sup>E. Ilisca and A. P. Legrand, Phys. Rev. B <u>5</u>, 4994 (1972).

<sup>7</sup>I. Solomon, Phys. Rev. 99, 559 (1955).

<sup>8</sup>I. Prigogine and G. Nicolis, J. Chem. Phys. <u>46</u>, 3542 (1967).

<sup>9</sup>P. Glansdorff and I. Prigogine, in *Structure*, *Stabilité et Fluctuations* (Masson, Paris, 1971).

<sup>10</sup>Chemically Induced Magnetic Polarization, edited by A. R. Lepley and G. L. Gloss (Wiley, New York, 1973).

## ERRATA

PHOTON STATISTICS AND SPECTRUM OF TRANSMITTED LIGHT IN OPTICAL BISTABIL-ITY. R. Bonifacio and L. A. Lugiato [Phys. Rev. Lett. 40, 1023 1978].

Equation (1) should read as follows:

 $Y = X + 2CX/(1 + X^2)$ .

We note that, in general, the ratio *R* between the height of the central peak and that of the sidebands well beyond the upper bistability threshold is given by

$$R = (\gamma_{\perp} + \gamma_{\parallel}) / \gamma_{\perp},$$

for the spectrum of both transmitted and fluorescent light. This gives R = 2 only if  $\gamma_{\parallel} = \gamma_{\perp}$ , whereas taking  $\gamma_{\parallel} = 2\gamma_{\perp}$  one finds the well-known result R = 3.

EXTENDED TIME-DEPENDENT HARTREE-FOCK APPROXIMATION WITH PARTICLE COLLISIONS. Cheuk-Yin Wong and Henry H. K. Tang [Phys. Rev. Lett. 40, 1070 (1978)].

In Eq. (5) on page 1071,  $g^{>}$  should read  $g^{<}$  and so Eq. (5) reads

$$-ig^{<}(x_{1},t_{1};x_{1}',t_{1}') = \sum_{\lambda}^{\infty} n_{\lambda}(T)\psi_{\lambda}(x_{1},t_{1})\psi_{\lambda}^{*}(x_{1}',t_{1}').$$
(5)

In Eq. (14) on page 1072, the last factor " $\langle 1, 2 | v' | 4, 3 - 3, 4 \rangle$ |<sup>2</sup>" should read " $\langle 1, 2 | v' | 4, 3 - 3, 4 \rangle$ ." In Eq. (18) on page 1072, a bracket after  $\theta(t - t_0)$  is missing. It should read

$$f(t) = \left\{ \left[ 1 + \left( \frac{Q_{20}}{a} \right)^2 \right] \exp\left[ \frac{1}{2} \pi a^2 G^2 \theta \left( t - t_0 \right) \right] - \left( \frac{Q_{20}}{a} \right)^2 \right\}^{-1/2}.$$
(18)

In Eq. (20) on page 1072, a division symbol in front of  $|d(E_A - E_B)/dt|$  is missing. Equation (20) should read

$$G^{2} = \frac{2}{\hbar} |\langle \mathbf{1}, \mathbf{2} | v' | \mathbf{4}, \mathbf{3} - \mathbf{3}, \mathbf{4} \rangle|^{2} \left| \frac{d}{dt} (E_{A} - E_{B}) \right|^{-1}.$$
(20)