

## Theoretical Rates and Correlation Functions in Ortho-Para H<sub>2</sub> Conversion on Paramagnetic Surfaces

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A theoretical study of ortho-para hydrogen conversion on paramagnetic surfaces is given. In the adsorbed layer, hydrogen molecules are assumed to behave like plane rotators, and their translation at the surface is described by means of a two-dimensional diffusion equation. The spatial dependence of the dipolar matrix elements is found to be important only in the close vicinity of surface impurities. Ortho-para time-correlation functions are computed, and their behavior is compared to the nuclear relaxation case. The total conversion probability is calculated, and two extreme cases are distinguished: (i) The ortho-para conversion energy goes to the thermal bath and the conversion rate is proportional to the diffusion constant and (ii) the ortho-para conversion energy goes to the spin impurity system. In contrast to Leffler's results, the best catalysts are found to be those which have the shortest impurity relaxation times.

### I. INTRODUCTION

Theoretical studies on ortho-para hydrogen conversion, at low temperature, have not been carried out during the last few years. The original theoretical approach was given by Wigner,<sup>1</sup> who stated that the strongly inhomogeneous magnetic field of paramagnetic impurities decouples the proton spins of the hydrogen molecule. As the speed of the conversion is directly related to the magnetic effective moment of the impurities, all experimental results were interpreted on the basis of this static theory. Wigner's study in liquids and gases is called homogeneous, in contrast to the heterogeneous study in which the magnetic impurities are located on a solid surface. Harrisson and MacDowell<sup>2</sup> extended Wigner's calculation to the heterogeneous case, which shall be referred to in the following, as the "classical theory."

It is necessary to provide a large amount of energy in order to convert a hydrogen molecule from a para to an ortho state. Nuclear and rotation states are coupled, and therefore, if  $h\omega_{op}$  is the so-called ortho-para energy,  $\omega_{op}$  is an "infrared" frequency ( $\omega_{op} \approx 5 \cdot 10^{12} \text{ sec}^{-1}$ ). According to the classical theory, the conversion energy is of kinetic origin. However, Leffler<sup>3</sup> suggested that this energy may be supplied by the spin relaxation of the surface magnetic impurities. The method used by Leffler is based on the calculation of the relaxation time of each proton of a hydrogen molecule located in the vicinity of a paramagnetic ion. The conversion rate is then obtained by the difference of the relaxation rates of the two protons. The conclusion

reached is that those paramagnetic ions having long relaxation times make the best catalysts. In fact, according to Pauli's principle, nuclear and rotation states are coupled, and therefore Leffler's treatment is inaccurate.

In this work, a theoretical study is provided of the conversion in the adsorbed layer and of the influence of the spin relaxation time of the impurities located on the surface of the catalyst. A short account of this theory has already been given for both paramagnetic and ferromagnetic catalysts.<sup>4</sup>

A simple theoretical model, built from experimental results, is described in Sec. II. In Sec. III, basic equations are derived for the various ortho-para transitions and for the total conversion rate. In Sec. IV, time and spatial dependences are discussed and numerical applications are given. In Sec. V, numerous theoretical rates are calculated and the influence of the spin relaxation is discussed.

### II. MODEL

The ortho-para transition probabilities and the total conversion rate are calculated by choosing a simple model satisfying the following five assumptions (the first two indicate the rotational motion of the molecule at the surface; the third and fourth ones, its translational motion; the last one, the surface impurity locations and their spin relaxation times).

(i) At low temperatures,  $T < 100 \text{ }^\circ\text{K}$ , only the two lowest ortho and para ground states are populated (at  $T = 100 \text{ }^\circ\text{K}$  about 99% of the molecules are in the  $J = 0$  and  $J = 1$  states,  $J$  being the rotational quantum number). Only these two ground states will be taken

into consideration.

(ii) When a hydrogen molecule is adsorbed, its rotational motion is seriously altered by the surface, which introduces a potential barrier restricting the turning over of the molecule. In the case of a high barrier or of a low temperature, the two rotational degrees of freedom will become effectively one degree of planar rotation [around an axis ( $\hat{O}z$ ) perpendicular to the surface].

White<sup>5</sup> developed a theory in which the interaction potential between the adsorbed molecule and the surface is described by a Morse-type function. Parameters were calculated and compared to the experimental results of Cunningham *et al.*<sup>6</sup> A conclusion is reached that adsorbed hydrogen molecules behave approximately as plane rotators. Consequently, in the following, we assume that hydrogen molecules are free to rotate in a plane parallel to the surface, the rotational ortho wave functions being equal to  $\psi_o^\nu = [1/(2\pi)^{1/2}]e^{-i\nu\phi}$ , where  $\nu = \pm 1$  and  $\phi$  is the rotational angle about the  $z$  axis perpendicular to the surface ( $\psi_o^\nu$  are eigenfunctions of  $J^z$ ).

(iii) During their stay on the catalyst surface, the molecules will travel over no more than 100 Å. It is therefore assumed that the surface of the catalyst is planar. At low temperatures, the adsorbed mono layer is almost completely filled and behaves as a two-dimensional ideal gas, which is the hypothesis of supermobile adsorption. In such a case the translational motion is described by a two-dimensional diffusion equation. We use the theory of random walk in a way similar to that of Torrey<sup>7</sup> for nuclear relaxation.

(iv) When the molecule receives enough energy from the solid (phonons) or from the gas (collision with another molecule), it leaves the surface. According to Cunningham and Johnston's experimental results,<sup>8</sup> the exchange of molecules between the bulk and the adsorbed phase is assumed to be slow compared to the conversion speed. The internal vibrational degree is not perturbed, as the forces introduced by the surface are rather small compared to the restoring forces involved in the internal vibration.<sup>9</sup>

(v) The assumption is made that some magnetic impurities are located very close to the surface and randomly dispersed and that their relaxation is isotropic. Following Bloembergen and Morgan,<sup>10</sup> we assume an exponential decrease for the correlation function:

$$\langle S_\alpha(t) S_\alpha(t + \tau) \rangle = \frac{1}{3} S(S+1) e^{-\tau/\tau_p} \delta_{\alpha, \alpha'},$$

where  $S(t)$  is the time dependence of the spin orientation of a surface impurity ( $S$  being treated as a semiclassical variable;  $\alpha = x, y, z$ ) and  $\tau_p$  is the isotropic relaxation time.

### III. THEORETICAL RATES

We start with an unperturbed Hamiltonian  $H_0 = M + R$ , where  $M$  is the part of the Hamiltonian  $H_0$  which describes the internal states and energies of an adsorbed hydrogen molecule. Let  $|\phi^\mu\rangle$  be its nuclear eigenfunctions and  $|\psi^\nu\rangle$  its rotational eigenfunctions (see the Appendix).  $o$  and  $p$  are the indices of an ortho and para state and  $|\Lambda^{\mu\nu}\rangle = |\Phi^{\mu\nu}\rangle$ .

$R$  is the part of the Hamiltonian  $H_0$  which describes the impurity spin system and the motion of the molecule on the catalyst surface. Let  $|\Theta\rangle$  be its eigenstates.

We introduce a perturbing Hamiltonian  $H_1$  which describes the dipole-dipole interaction connecting the spin magnetic impurity  $\vec{S}$  with the two protons of the adsorbed hydrogen molecule. Thus symmetry is broken, and ortho and para states are slightly mixed. In the interaction representation, the time dependence is introduced as follows:

$$H_1(t) = e^{i(M+R)t} H_1 e^{-i(M+R)t} \quad (1)$$

The transition probability from an initial ortho state  $|\Lambda_o^{\mu\nu}\rangle|\Theta_i\rangle$  to a final para state  $|\Lambda_p\rangle|\Theta_f\rangle$  may be written

$$W_{i,f}^{\mu\nu} = \frac{1}{\hbar^2} \int_0^\infty \langle \Lambda_p \Theta_f | H_1(t) | \Theta_i \Lambda_o^{\mu\nu} \rangle \times \langle \Lambda_o^{\mu\nu} \Theta_i | H_1(t') | \Lambda_p \Theta_f \rangle dt' + c. c. \quad (2)$$

If we define

$$A_{\mu\nu} = \langle \Lambda_o^{\mu\nu} | H_1 | \Lambda_p \rangle, \quad A_{\mu\nu}(t) = e^{iRt} A_{\mu\nu} e^{-iRt},$$

Eq. (2) is found to be

$$W_{i,f}^{\mu\nu} = \frac{1}{\hbar^2} \int_0^\infty \langle \Theta_f | A_{\mu\nu}(t) | \Theta_i \rangle \langle \Theta_i | A_{\mu\nu}(t - \tau) | \Theta_f \rangle \times e^{-i\omega_{op}\tau} d\tau + c. c., \quad (3)$$

where  $\hbar\omega_{op} = E_o - E_p$  is the ortho-para energy. The transition probability from the para ground state to an almost degenerate ortho ground state equals

$$W_{op}^{\mu\nu} = \sum_{i,f} P(\Theta_i) W_{i,f}^{\mu\nu}, \quad (4)$$

$P(\Theta_i)$  being the probability of finding the system in the state  $|\Theta_i\rangle$ . Owing to energy conservation, the eigenvalues  $E_i$  and  $E_f$ , corresponding to the  $|\Theta_i\rangle$  and  $|\Theta_f\rangle$  states, must satisfy

$$E_f - E_i = \hbar\omega_{op}, \quad (5)$$

and thus summations on  $i$  and  $f$  of Eq. (4) are restricted by Eq. (5). Let the quantum correlation function relative to the catalyst and to the motion of the molecule on the surface  $g_{\mu\nu}(\tau)$  be defined by

$$g_{\mu\nu}(\tau) = \sum_{i,f} P(\Theta_i) \langle \Theta_f | A_{\mu\nu}(t) | \Theta_i \rangle \langle \Theta_i | A_{\mu\nu}(t - \tau) | \Theta_f \rangle. \quad (6)$$

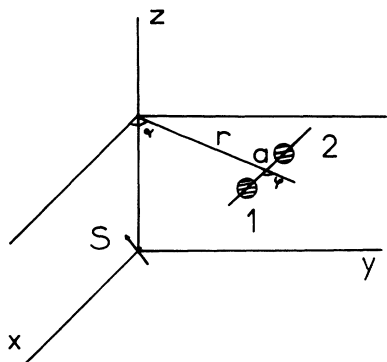


FIG. 1. Hydrogen molecule in the close vicinity of a magnetic impurity. The distance  $\vec{R}$  between the molecule and the impurity is defined in cylindrical polar coordinates  $\vec{R}(\gamma, \alpha, z)$ ; the rotational angle is designated by  $\phi$ .

Then Eqs. (3) and (4) may be written

$$W_{op}^{\mu\nu} = \frac{1}{\hbar^2} \int_0^\infty g_{\mu\nu}(\tau) e^{-i\omega_{op}\tau} dt + \text{c. c.} , \quad (7)$$

which is the spectral density at the frequency  $\omega_{op}$ . The total conversion rate is given by

$$W_{op} = \sum_{\mu\nu} W_{op}^{\mu\nu} . \quad (8)$$

In the following, the quantum correlation function will be replaced by the classical one.

(i) The rotational and nuclear matrix elements  $A_{\mu\nu} = \langle \Lambda_\sigma^{\mu\nu} | H_1 | \Lambda_\rho \rangle$  are calculated as functions of the position of the molecule and the spin components.

(ii) The position  $\vec{R}$  and the spin  $\vec{S}$  are now treated

as classical variables, time dependent, and, consequently,  $A_{\mu\nu}$  dependent too. Thus, we are able to compute the new classical correlation functions  $g_{\mu\nu}(t) = \langle A_{\mu\nu}(0) A_{\mu\nu}(t) \rangle$  by taking into account the assumptions made in Sec. II.

(iii) The ortho-para transition probabilities and the total conversion rate, which are given by Eqs. (7) and (8), are then deduced.

#### IV. SPATIAL AND TIME DEPENDENCES

##### A. Spatial Dependence of Nuclear and Rotational Matrix Elements

The matrix elements  $A_{\mu\nu}$  are calculated in the Appendix. They may be written

$$A_{\mu\nu} = \sum_{\alpha\beta} D_{\mu\nu}^{\alpha\beta} S_\alpha \sigma_\beta , \quad (9)$$

where  $D_{\mu\nu}^{\alpha\beta}$  are constants,  $S_\alpha$  the components of  $\vec{S}$ , and  $\sigma_\beta$  functions of the distance  $\vec{R}$  between the center of the molecule and the magnetic spin, which is expressed in cylindrical polar coordinates  $(\vec{r}, z)$  as shown in Fig. 1. The surface plane is given by  $z=0$  and the plane in which the molecule moves by  $z$ . The functions  $\sigma_\beta(\vec{r}, z)$ , calculated in the Appendix, were numerically computed for  $\alpha=0$ ,  $z=2 \text{ \AA}$  (Fig. 2) and  $z=2.5 \text{ \AA}$  (Fig. 3). This calls for the following comments.

(i) Every  $\sigma_\beta$  function has a specific spatial dependence. For instance, only the function  $\sigma_2$  differs from zero at  $r=0$ . In the case of strongly localized adsorption in the close vicinity of  $r=0$ , the spatial dependence of  $A_{\mu\nu}$  will be dominated by the  $\sigma_2$  one. In the case of mobile adsorption, the average has to be taken over the  $\sigma_\beta$  functions

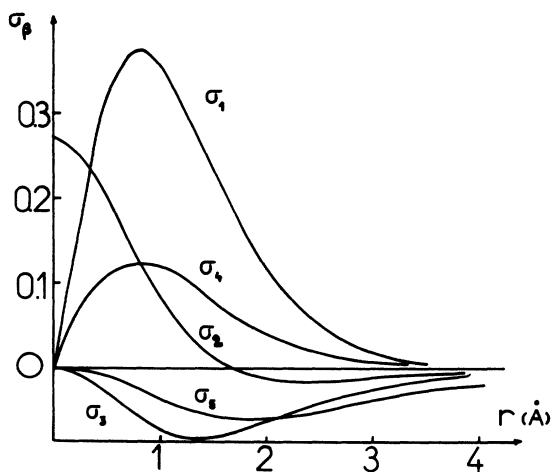


FIG. 2. The spatial dependence  $\sigma_\beta(\vec{R})$  of the nuclear and rotational matrix elements is represented for  $z=2 \text{ \AA}$  and  $\alpha=0$ . The ordinate  $\sigma_\beta$  is expressed in  $10^{27}$  cgs units. (Detailed expressions are given in the Appendix.)

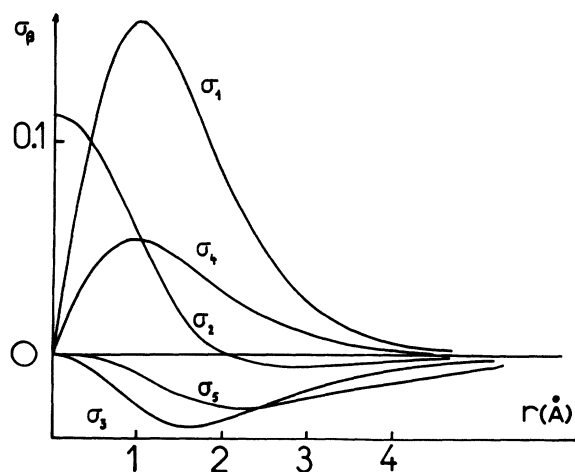


FIG. 3. The spatial dependence  $\sigma_\beta(\vec{R})$  of the nuclear and rotational matrix elements are represented for  $z=2.5 \text{ \AA}$  and  $\alpha=0$ . The ordinate  $\sigma_\beta$  is expressed in  $10^{27}$  cgs units. (Detailed expressions are given in the Appendix.)

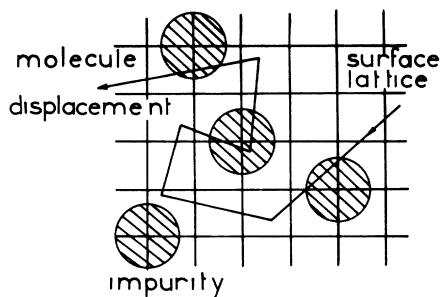


FIG. 4. The surface plane contains, all around each impurity, what could be called a conversion disk of radius approximately equal to 4 Å. During its stay on the surface, the hydrogen molecules "walk" through these disks, where they are converted.

as in Sec. IV B.

(ii)  $\sigma_\beta$  becomes negligible when  $z > 2.5$  Å. Therefore, only the first adsorbed layer can be converted and only the impurities located on the surface of the catalyst can convert. Inversely, experiments where ortho-para hydrogen conversion is measured prove the existence of impurities on the catalyst surface.

(iii)  $\sigma_\beta$  become negligible when  $r > 4$  Å. Therefore the hydrogen molecule must be close to the impurity to be converted. Moreover, a molecule has some probability to be converted only by a single impurity at a time (Fig. 4). Conversion is a microscopic phenomenon, in contrast to nuclear relaxation, where the molecules are relaxed by a great number of the catalyst surface (and near-surface) impurities. Consequently, conversion gives direct information on the average behavior of a single impurity and on the surface impurity concentration.

#### B. Time-Correlation Functions

We turn now to the calculation of the time-correlation functions  $g_{\mu\nu}(t) = \langle A_{\mu\nu}(0)A_{\mu\nu}(t) \rangle$ , where  $A_{\mu\nu}$  is given by Eq. (9), and where  $\vec{S}$  and  $\vec{R}$  are treated as time-dependent classical variables. Furthermore, we make the approximation that there is no correlation between the motion of the adsorbed hydrogen molecules and the spin relaxation of the surface impurities. Thus,

$$g_{\mu\nu}(t) = \sum_{\substack{\alpha\beta \\ \alpha'\beta'}} D_{\mu\nu}^{\alpha\beta} D_{\mu\nu}^{\alpha'\beta'} \langle S_\alpha(0)S_{\alpha'}(t) \rangle \langle \sigma_\beta(0)\sigma_{\beta'}(t) \rangle. \quad (10)$$

According to assumption (5), Eq. (10) is reduced to the calculation of the new time-correlation functions

$$G_{\beta\beta'}(t) = \langle \sigma_\beta(0)\sigma_{\beta'}(t) \rangle,$$

which are calculated by means of the random-walk theory applied by Torrey<sup>7</sup> and Kokin and Izmistiev<sup>11</sup>

to nuclear magnetic relaxation in adsorbed layers. Describing the adsorbed-molecules displacement by a two-dimensional translational diffusion equation, the correlation functions  $G_{\beta\beta'}$  may be written

$$G_{\beta\beta'} = \frac{1}{(2\pi)^2} \iint d\vec{r}_0 d\vec{r} \sigma_\beta(\vec{r}_0) \sigma_{\beta'}(\vec{r}) \times \int \exp[-2k^2Dt + ik(r-r_0)] d^2k, \quad (11)$$

where  $D$  is the diffusion constant. If we set

$$\sigma_\beta(\vec{r}) = \rho_\beta(r) e^{im\alpha}, \quad \sigma_{\beta'}(\vec{r}) = \rho_{\beta'}(r) e^{in\alpha},$$

it is found that

$$G_{\beta\beta'} = 2\pi \sum_l \int k dk e^{-2k^2Dt} \int \int J_l(kr) J_l(kr_0) \times \rho_\beta(r) \rho_{\beta'}(r_0) r dr r_0 dr_0 \delta_{l,m} \delta_{l,-n}, \quad (12)$$

where  $J_l$  is the Bessel function of  $l$  order. New selection rules are introduced by the factors  $\delta_{l,m}$  and  $\delta_{l,-n}$ . The correlation functions which figure in Eq. (10) and differ from zero are  $G_{11}$ ,  $G_{22}$ ,  $G_{33}$ ,  $G_{44}$ , and  $G_{55}$ , given by Eq. (12). They have been computed and are represented in Fig. 5. One may note the following:

$$(a) G_{11} \gg G_{33} \gg G_{55} > G_{22}, G_{44};$$

$$G_{55} \gg G_{44}.$$

In the case of isotropic relaxation, we may neglect all  $G_{\beta\beta}$  in front of  $G_{11}$ .

(b) If our results are compared to those, concerning nuclear relaxation, of Kokin and Izmistiev<sup>11</sup> and Beckett,<sup>12</sup> it may be observed that our functions  $G_{\beta\beta}$  decrease comparatively more slowly. Thus it is deduced that, for ortho-para conversion in adsorbed phases, molecules are more strongly correlated than for relaxation. This can be explained by the fact that the functions  $\sigma_\beta(\vec{R})$  have a shorter spatial range than the ones encountered in nuclear relaxation.

(c) In the following,  $G_{11}$  will be approximated by an exponential time decrease  $G_{11} \approx e^{-t/\tau_c}$ , where the translational correlation time  $\tau_c$  is defined by  $\tau_c = r_0^2/16D$ , with  $r_0$  being the radius of the conversion disk ( $r_0 \approx 4$  Å). In fact,  $G_{11}$  decreases more slowly than an exponential, but the results are not qualitatively changed by this approximation. Fol-

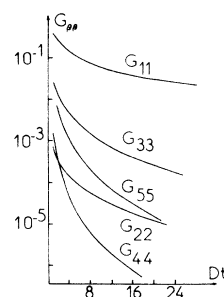


FIG. 5. Time-correlation function  $G_{\beta\beta}$  of  $\sigma_\beta(\vec{R})$  when the displacement of the hydrogen molecules, adsorbed in a monomolecular layer, is described by a diffusion equation. ( $D$  is expressed in  $\text{cm}^2/\text{sec}$  and the time  $t$  in sec.)

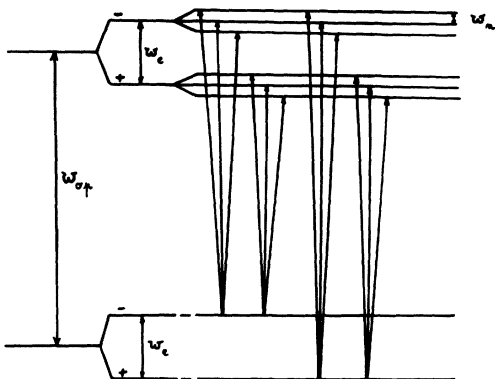


FIG. 6. Ortho-para transitions when a low magnetic field is applied.  $\omega_e$  and  $\omega_n$  are the electronic and nuclear Zeeman energies. The total nuclear spin  $I$  of an ortho state equals 1 and the electronic impurity spin  $S$  is chosen equal to  $\frac{1}{2}$ .

lowing (a), Eq. (10) may be written

$$\sum_{\nu} g_{\pm 1\nu}(t) = \frac{3}{8} G_{33} \langle S_x(0) S_x(t) \rangle + \frac{1}{8} G_{11} \langle S^+(0) S^-(t) \rangle, \quad (13a)$$

$$\sum_{\nu} g_{0\nu}(t) = 4 G_{11} \langle S_x(0) S_x(t) \rangle + \frac{3}{2} G_{33} \langle S^+(0) S^-(t) \rangle. \quad (13b)$$

#### V. ORTHO-PARA TRANSITIONS AND TOTAL CONVERSION RATE

The twelve ortho-para transitions, which are outlined in Fig. 6, may be divided into four cases, according to the conservation, or lack of conservation, of the electronic and nuclear longitudinal spin components  $S_x$  and  $I_x$ . The numerical transition probabilities may be calculated by using Eqs. (7) and (13). It is easily seen, from Eqs. (13) and remark (a), that the most important transition probability is the one which conserves both  $S_x$  and  $I_x$ , i. e.,

$$h^{-2} \int 4G_{11} \langle S_x(0) S_x(t) \rangle e^{-i\omega_{op}t} dt. \quad (14)$$

The next, being the one which changes both  $S_x$  and  $I_x$ , is 16 times less. Thus it may be neglected, as well as the others. Therefore, by taking into account assumption (5), Eqs. (6) and (7), and remark (c), the total conversion rate, which is approximately given by the transition probability (14), is proportional to

$$W_{op} \sim 2\tau / (1 + \omega_{op}^2 \tau^2), \quad (15a)$$

where

$$1/\tau = 1/\tau_c + 1/\tau_p. \quad (15b)$$

It is of interest to distinguish between three different cases, as follows.

$$A. \tau_p \gg \tau_c$$

This case is the one encountered in the usual

classical theory and corresponds to a fast motion of the molecules on the catalyst surface or to a slow relaxation of the surface impurities.

Equation (15a) becomes

$$W_{op} \sim 2\tau_c / (1 + \omega_{op}^2 \tau_c^2). \quad (16)$$

The conversion rate is maximum for  $\omega_{op}\tau_c = 1$ , which gives  $\tau_c = 10^{-12}$  sec (as  $\omega_{op} = 10^{12}$  sec $^{-1}$ ). In fact, usually  $\tau_c \gg 10^{-12}$  sec, and thus the conversion rates are less than  $10^{-2}$  of their theoretical maximum. In such a case the main result is that the transition probability  $W_{op}$  is inversely proportional to  $\tau_c$  and directly proportional to the diffusion constant  $D$  of the adsorbed hydrogen molecules.

The ortho-para energy  $\omega_{op}$  is transferred to the thermal bath via the kinetic energy of the adsorbed phase.

$$B. \tau_p \ll \tau_c$$

This case, considered by Leffler,<sup>3</sup> corresponds to a fast relaxation of the surface impurities. Equation (15a) becomes

$$W_{op} \sim 2\tau_p / (1 + \omega_{op}^2 \tau_p^2). \quad (17)$$

The conversion rate is maximum for  $\tau_p = 10^{-12}$  sec, which is rarely verified. Nevertheless, paramagnetic relaxation times, which check with  $\tau_p \ll \tau_c$ , do exist in the range  $10^{-8} < \tau_p < 10^{-12}$  sec, and therefore  $W_{op} \sim \tau_p^{-1}$ . In such a case, the electronic spin relaxation of the surface impurities converts ortho hydrogen into para hydrogen, the ortho-para conversion energy going to the solid lattice via the spin system. The shorter  $\tau_p$  is, the faster the conversion.

$$C. \tau_p \cong \tau_c$$

$W_{op}$  is given by Eq. (15). The ortho-para energy is divided in two parts. The first goes to the thermal bath, the second one to the spin system, approximately in the same proportions as  $\tau_p$  compared to  $\tau_c$ .

The three cases A–C may be successively encountered during the same experiment by varying, for instance, the temperature.

It may be concluded that, besides its theoretical interest, ortho-para hydrogen conversion could be used in the study of the magnetic catalyst surfaces and could give more precise information than, for example, nuclear relaxation on these surfaces. Moreover, it has been indicated that in some cases the electronic spin relaxation of the surface impurities converts ortho hydrogen into para hydrogen. In these cases, in contrast to Leffler's results, the best catalysts are those which have the shortest impurity relaxation times.

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#### APPENDIX: MATRIX ELEMENTS $A_{\mu\nu}$

We have

$$A_{\mu\nu} = \langle \Phi_\rho \psi_\rho | H_1 | \Phi_\sigma^\mu \psi_\sigma^\nu \rangle.$$

The wave functions are composed of (i) the rotational wave functions  $|\psi\rangle$ :

$$\text{ortho state } J=1, \quad |\psi_o^\nu\rangle = (2\pi)^{-1/2} e^{i\nu\phi}$$

$$\text{para state } J=0, \quad |\psi_p\rangle = (2\pi)^{-1/2},$$

and (ii) the nuclear wave functions  $|\Phi\rangle$ :

$$\text{ortho state } I=1, \quad |\Phi_o^\mu\rangle = \begin{cases} |++\rangle \\ (1/\sqrt{2})\{|+-\rangle + |-+\rangle\} \\ |--\rangle \end{cases}$$

$$\text{para state } I=0, \quad |\Phi_p\rangle = (1/\sqrt{2})\{|+-\rangle - |-+\rangle\}.$$

$H_1$  is the perturbing Hamiltonian describing the dipolar interaction between the spin impurity  $S$  and the two protons of the hydrogen molecule. The six matrix elements are thus found equal to<sup>13</sup>

$$A_{11} = \frac{\mu_e \mu_p}{2\pi\sqrt{2}} \left( \frac{1}{4} S^+ \sigma_1 + \frac{3}{2} S_x \sigma_3^* + \frac{3}{4} S^- \sigma_3^* \right),$$

$$A_{1-1} = \frac{\mu_e \mu_p}{2\pi\sqrt{2}} \left( \frac{1}{4} S^+ \sigma_1 + \frac{3}{2} S_x \sigma_2 + \frac{3}{4} S^- \sigma_4 \right),$$

$$A_{-11} = \frac{\mu_e \mu_p}{2\pi\sqrt{2}} \left( -\frac{1}{4} S^- \sigma_1 - \frac{3}{2} S_x \sigma_2^* - \frac{3}{4} S^+ \sigma_4^* \right),$$

$$A_{-1-1} = \frac{\mu_e \mu_p}{2\pi\sqrt{2}} \left( -\frac{1}{4} S^- \sigma_1 - \frac{3}{2} S_x \sigma_3 - \frac{3}{4} S^+ \sigma_5 \right),$$

$$A_{01} = \frac{\mu_e \mu_p}{2\pi} \left( S_x \sigma_1 - \frac{3}{2} S^- \sigma_3^* - \frac{3}{2} S^+ \sigma_3^* \right),$$

$$A_{0-1} = \frac{\mu_e \mu_p}{2\pi} \left( S_x \sigma_1 - \frac{3}{2} S^- \sigma_2 - \frac{3}{2} S^+ \sigma_3 \right),$$

with the following notations:

$$f_1 = \frac{r_1^2 - 3z_1^2}{r_1^5} - \frac{r_2^2 - 3z_2^2}{r_2^5},$$

$$f_2 = ze^{i\alpha} \left( \frac{x_1^+}{r_1^3} - \frac{x_2^+}{r_2^3} \right) = f_3^*,$$

$$f_4 = e^{2i\alpha} \left( \frac{x_1^{+2}}{r_1^5} - \frac{x_2^{+2}}{r_2^5} \right) = f_5^*,$$

and

$$\sigma_B = \int f_B e^{-i\phi} d\Phi.$$

$\mu_e$  is the electronic magnetic moment of the spin impurity  $\bar{S}$  and  $\mu_p$  the nuclear magnetic moment of the spin  $I$  of an hydrogen molecule proton.

The expressions for  $\sigma_B$  are the following:

$$\sigma_1 = \frac{4}{(2ar)^{3/2}} (I_{1/2} - bI_{3/2}) - \frac{12z^2}{(2ar)^{5/2}} (I_{3/2} - bI_{5/2}),$$

$$\sigma_2 = \left( \frac{4zr}{(2ar)^{5/2}} (I_{3/2} - bI_{5/2}) + \frac{4az}{(2ar)^{5/2}} I_{5/2} \right) e^{-i\alpha},$$

$$\sigma_3 = \left( \frac{4zr}{(2ar)^{5/2}} (I_{3/2} - bI_{5/2}) + \frac{4az}{(2ar)^{5/2}} (\lambda - I_{5/2}) \right) e^{i\alpha},$$

$$\sigma_4 = \left( \frac{4r^2}{(2ar)^{5/2}} (I_{3/2} - bI_{5/2}) + \frac{4I_{5/2}}{(2ar)^{3/2}} + \frac{4a^2}{(2ar)^{5/2}} \right. \\ \left. \times (I_{3/2} - bI_{5/2}) \right) e^{-2i\alpha},$$

$$\sigma_5 = \left( \frac{4r^2}{(2ar)^{5/2}} (I_{3/2} - bI_{5/2}) + \frac{4(\lambda - I_{5/2})}{(2ar)^{3/2}} + \frac{4a^2}{(2ar)^{5/2}} \right. \\ \left. \times (\mu - \nu) \right) e^{2i\alpha},$$

where  $I_{1/2}$ ,  $I_{3/2}$ ,  $I_{5/2}$ ,  $\lambda$ ,  $\mu$ , and  $\nu$  are known functions of elliptic integrals of the first and second kind,  $F(\frac{1}{2}\pi, q)$  and  $E(\frac{1}{2}\pi, q)$ , respectively, where  $q = \{4ar/[(a+r)^2 + z^2]\}^{1/2}$ . (See Fig. 1.)

<sup>1</sup>E. Wigner, Z. Physik. Chem. (Leipzig) **B23**, 28 (1933).

<sup>2</sup>L. G. Harrison and C. A. MacDowell, Proc. Roy. Soc. (London) **A220**, 77 (1953).

<sup>3</sup>A. J. Leffler, J. Chem. Phys. **43**, 4410 (1965).

<sup>4</sup>E. Ilisca, Phys. Rev. Letters **24**, 797 (1970).

<sup>5</sup>D. White, J. Chem. Phys. **32**, 72 (1960).

<sup>6</sup>C. M. Cunningham, D. S. Chapin, and H. L. Johnston, J. Am. Chem. Soc. **80**, 2382 (1958).

<sup>7</sup>H. C. Torrey, Phys. Rev. **92**, 962 (1953).

<sup>8</sup>C. M. Cunningham and H. L. Johnston, J. Am. Chem.

Soc. **80**, 2377 (1958).

<sup>9</sup>T. L. Hill, J. Chem. Phys. **16**, 181 (1948).

<sup>10</sup>N. Bloembergen and L. O. Morgan, J. Chem. Phys. **34**, 842 (1961).

<sup>11</sup>A. A. Kokin and A. A. Izmestiev, Zh. Fiz. Khim. **39**, 577 (1965) [Translated in J. Phys. Chem. **39**, 309 (1965)].

<sup>12</sup>D. Beckert, Ann. Physik **7**, 220 (1967).

<sup>13</sup>E. Ilisca, thesis (University of Paris, 1971) (CNRS Report No. 5704) (unpublished).