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THEORETICAL CALCULATION OF A NEW EFFECT IN ORTHO-PARA H₂ CONVERSION ON MAGNETIC SURFACES

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Evidence is presented for a new effect in ortho-para H₂ conversion on magnetic solid surfaces at low temperature. This effect is a resonant exchange of energy between the spins of the magnetic impurities and H₂ molecules which are adsorbed in their vicinity. This process could explain the strong activities of many catalysts.

In 1933 Wigner¹ calculated the effect of paramagnetic molecules on the ortho-para conversion rate of gaseous hydrogen. The coupling of the nuclear spins of a H₂ molecule with the dipole field of a nearby magnetic molecule breaks the symmetry and causes a slight mixing of ortho and para states. Kinetic energy provides the energy balance. The same mechanism was used in 1953 by Harrison and McDowell² in a calculation for the heterogeneous case in which the magnetic dipoles are part of a solid surface on which the H₂ molecules are adsorbed. At temperatures below 100°K the more effective magnetic catalysts have conversion rates which are up to 10⁴ times those calculated.³ This discrepancy can be removed when one allows for the possibility that the energy balance is provided by magnons.

The ortho-para transition probability is proportional to the spectral density $J(\omega)$ of the matrix element of the perturbation, H_1 , at the frequency $\omega_{op} = (E_o - E_p)/\hbar$, where E_o and E_p are the energies of the lowest ortho and para states of an adsorbed H₂ molecule. H_1 is the sum of the dipole interactions of the magnetic spin \vec{S} with the two protons of this molecule. Let $A_{\mu\nu}$ be the part of H_1 connecting the para (ground) state (total nuclear spin zero, rotational angular momentum zero) and one of the almost degenerate ortho

ground states (nuclear spin state μ , rotational state ν). $A_{\mu\nu}$ depends on \vec{S} and on the distance \vec{R} between the molecule and the magnetic spin. It is of the form

$$A_{\mu\nu} = \sum_{\alpha\beta} D_{\mu\nu}^{\alpha\beta} S_{\alpha} \rho_{\beta}, \quad (1)$$

where $D_{\mu\nu}^{\alpha\beta}$ are constants, S_{α} are the components of \vec{S} , and ρ_{β} are known functions of \vec{R} . One has

$$J(\omega) = \sum_{\mu\nu} \int_0^{\infty} \langle A_{\mu\nu}(0) A_{\mu\nu}(t) \rangle e^{-i\omega t} dt + c.c., \quad (2)$$

where $A_{\mu\nu}(t)$ is the operator in the interaction representation, and where $\langle \rangle$ indicates the average over a canonical ensemble for the magnetic spin variables and the position variables. Neglecting correlation between the time dependence of \vec{S} and \vec{R} , one has

$$\begin{aligned} \langle A_{\mu\nu}(0) A_{\mu\nu}(t) \rangle &= \sum_{\alpha\beta\alpha'\beta'} D_{\mu\nu}^{\alpha\beta} D_{\mu\nu}^{\alpha'\beta'} \\ &\times \langle S_{\alpha}(0) S_{\alpha'}(t) \rangle \langle \rho_{\beta}(0) \rho_{\beta'}(t) \rangle. \end{aligned} \quad (3)$$

Furthermore, the approximation is made that the time dependence of \vec{R} is characterized by a correlation time τ_c , i.e.,

$$\langle \rho_{\beta}(0) \rho_{\beta'}(t) \rangle = K_{\beta\beta'} e^{-t/\tau_c}. \quad (4)$$

The form of the spin correlation function depends on the interactions of the magnetic spins with the lattice and with each other. Two cases are dis-

cussed here.

I. For a paramagnetic catalyst one has typically

$$\langle S_{\alpha}(0)S_{\alpha'}(t) \rangle = \frac{S(S+1)}{3} \delta_{\alpha\alpha'} e^{-t/\tau_p}, \quad (5)$$

where τ_p is the relaxation time of the magnetic spin. Thus

$$J(\omega_{op}) \sim \frac{2\tau}{1 + \omega_{op}^2 \tau^2}, \quad (6)$$

where $\tau^{-1} = \tau_p^{-1} + \tau_c^{-1}$. As a function of τ , the conversion rate reaches its maximum when $\omega_{op}\tau = 1$, which gives $\tau \approx 10^{-12}$ sec. It is of interest to distinguish between the case $\tau_c \ll \tau_p$ and $\tau_c \gg \tau_p$.

(a) $\tau_c \ll \tau_p$. This is the case considered in Ref. 2; the ortho-para energy difference is transferred to the H_2 thermal bath via the kinetic energy of the adsorbed phase. As τ_c for adsorbed hydrogen at $T < 100^\circ\text{K}$ is typically of the order of 10^{-10} sec or longer, the conversion rate is less than 10^{-2} of its theoretical maximum. Because of $\omega_{op}\tau_c \gg 1$, $J(\omega_{op}) \sim 1/\tau_c$, i.e., the conversion rate increases with increasing temperature.

(b) $\tau_c \gg \tau_p$. In this case the energy goes to the solid lattice, via the spin system. Paramagnetic relaxation times of 10^{-10} sec and shorter do exist, even at low temperatures. For such systems, spins with shorter relaxation times give larger conversion rates. Leffler⁴ reached the opposite conclusion.

II. With a Heisenberg ferromagnet as catalyst, one has, for components perpendicular to the spontaneous magnetization,

$$\langle S_{\alpha}(0)S_{\alpha}(t) \rangle \sim \sum_{\vec{q}} [F(\omega_{\vec{q}}) - F(-\omega_{\vec{q}})], \quad (7)$$

where

$$F(\omega_{\vec{q}}) = n(\omega_{\vec{q}}) e^{-t(i\omega_{\vec{q}} + 1/\tau_{\vec{q}})}. \quad (8)$$

$\omega_{\vec{q}}$ is the frequency of a magnon with wave number \vec{q} , $\tau_{\vec{q}}$ is its lifetime, and $n(\omega_{\vec{q}})$ its distribution function, i.e., $n(\omega) = (e^{\omega/kT} - 1)^{-1}$. When $f(\omega)$ denotes the density of magnon states, one there-

fore has

$$J(\omega_{op}) \sim \int_0^{\infty} d\omega f(\omega) n(\omega) [B(\tau, \omega_{op} - \omega) - B(\tau, \omega_{op} + \omega)], \quad (9)$$

where the constant of proportionality is of the same order as in (6) and where

$$B(\tau, \omega) = \frac{2\tau}{1 + \omega^2 \tau^2}, \quad \tau(\omega_{\vec{q}})^{-1} = \tau_c^{-1} + \tau_{\vec{q}}^{-1}. \quad (10)$$

The first term in the square brackets of Eq. (9) displays a sharp resonance: Given that, at low T , $\omega_{op}\tau \gg 10^2$, one has $B(\tau, 0)/B(\tau, \omega_{op}) \gg 10^4$. Therefore, one can approximate:

$$J(\omega_{op}) \sim n(\omega_{op}) \bar{f}(\omega_{op}), \quad (11)$$

where $\bar{f}(\omega_{op})$ is the average of $f(\omega)$ over a region of width $1/\tau$ around ω_{op} . As the density of magnon states is narrowly peaked, (11) can be several orders of magnitude larger than (6) provided that the peak falls within a width $1/\tau$ of ω_{op} , which requires a Curie temperature of the order of 100°K . Under this condition, larger values of τ (lower T) give larger conversion rates. The ortho-para energy difference is principally used to excite a single magnon.

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