New Channel in Ortho-Para Hydrogen Conversion

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A new channel in ortho-para hydrogen conversion is suggested as a tenative interpretation of large experimental reaction rates. This process occurs in two steps, via a virtually excited electronic state. The first step involves an exchange of electrons between the molecule and a nearby magnetic impurity while the second step is due to the hyperfine contact interaction between the virtually excited electronic spin of the molecule and its nuclear spins. This new process turns out to be more effective than the Wigner one if the exchange interaction exceeds a moderate value.

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Orthohydrogen and parahydrogen (o-H_2,p-H_2) considered as two varieties of molecular hydrogen, are associated with the early history of quantum mechanics. Since then, a tremendous number of o-p-H_2 conversion experiments have been performed. The magnetic mechanism proposed by Wigner in 1933[1] is considered as a prototype of physical catalysis and is naturally distinguished from the simple chemical reaction where the two protons dissociate and recombine, as, for example, on metallic surfaces. Let us concentrate on the magnetic process. As solid catalysts, oxides provide a natural framework for the experimental test of the theory. Diluted impurities of chromia in an alumina support have been extensively considered,[2,3] as well as the whole series of sesquioxides of the rare earths supported (or not) on the diamagnetic lanthana.[4,5] For all oxides, the observed rates are found to be around 2 orders of magnitude larger than the theoretical rates, as deduced from the Wigner model.[2,4] Although it would be possible to account for this discrepancy by adjustment of the kinetics of molecular adsorption (an increase of the sticking time, for example), the parameter values that fit the experimental results seem unlikely. We therefore suggest an alternative channel for the magnetic o-p-H_2 conversion based on the virtual excitation of a magnetic molecular electronic state.

As the H_2 ground state has no electron spin, the magnetic Wigner mechanism for o-p conversion[1,6-10] is due to a hyperfine dipolar interaction between an external impurity spin and the two H_2 nuclear spins. The inhomogeneous magnetic field, created by the impurity, produces a relative dephasing in the precession of the two nuclear spins. This mechanism is effective as it satisfies the two needed selection rules

$$\Delta L \text{ odd}, \tag{1}$$

$$\Delta I = 1, \tag{2}$$

imposed by Pauli's principle, where L and I are the rotational and spin quantum numbers of the two nuclei. In this, hereafter labeled W, process, the selection rules (1) and (2) are simultaneously satisfied in one step, whereas we suggest that two-step processes, in which (1) and (2) are successively satisfied, may be at least as effective as the former. The first step, X, induces a virtual electronic transition due to an exchange coupling between the impurity electrons and those of the H_2 molecule. This singlet-triplet transition introduces an electronic spin in the molecular intermediate state and allows the second step, Y, to occur: an intramolecular hyperfine contact interaction between the electronic and nuclear spins of H_2. The order of these two steps may be interchanged.

In the following we give an example (H_2 on chromia) of this, hereafter labeled XY, process to illustrate its main features. We restrict the discussion to the first, ${}^3\Sigma_u^+$, excited state of H_2 as the intermediate state and to the ${}^4A_2$ ground state of Cr^{+++} paramagnetic impurity exposed to a crystal field of cubic symmetry. The instability of the ${}^3\Sigma_u^+$ state will not interfere, as the transition ${}^1\Sigma_g^+ \leftrightarrow {}^3\Sigma_u^+$ is virtual and occurs with a fixed internuclear distance. If we apply second-order time-dependent perturbation theory, and denote the exchange and hyperfine Hamiltonians by $\mathcal{X}$ and $\mathcal{Y}_c$, the para → ortho transition probability for this XY reaction path is written as

$$\mathcal{P}_{p\to\sigma}(XY) \sim \sum_{\beta,\gamma} \left| \sum_{\alpha} \langle {}^4A_2\,{}^1\Sigma_g^+ o \,|\, \mathcal{X} \,|\, {}^4A_2\,{}^3\Sigma_u^+ o \rangle \langle {}^3\Sigma_u^+ o \,|\, \mathcal{Y}_c \,|\, {}^1\Sigma_g^+ p \rangle / \Delta_e + (\mathcal{X} \leftrightarrow \mathcal{Y}_c) \right|^2 J_X(\omega_{op}), \tag{3}$$

where α, β, and γ denote the intermediate, initial, and final states of our quantum system, Δ_e stands for the energy difference $E({}^3\Sigma_u^+) - E({}^1\Sigma_g^+)$, and $J_X(\omega_{op})$ is some spectral density of the process at the o-p frequency ω_{op}. Para (p) and ortho (o) states are defined here as the singlet ($I=0$) and triplet ($I=1$) states.[11] All matrix elements are calculated within the ${}^4A_2$ Cr^{+++} ground state.

The exchange step is evaluated at some molecule-impurity mean distance. In the chromia electronic ground state, the three $3d$ electrons are accommodated in the t_{2g} shell, giving rise to the ${}^4A_2$ term. Its eigenfunctions are constructed from normalized Slater determinants of spin orbitals,[12] e.g., $\Psi(t_{2g}^3, {}^4A_2, m_s = \frac{3}{2}) = -|\xi\eta\zeta|$, where ξ, η, and ζ are the three orbitals (with spin up), base functions of t_{2g}, with lobes along the six (110) diagonals. The eigenfunctions of the molecular ground and excited states are similarly written as determinants of molecular spin orbitals, e.g., $\Psi({}^1\Sigma_g^+) = |g\bar{g}|$, $\Psi({}^3\Sigma_u^+, m_\sigma = 1) = |gu|$, where $g \equiv (\sigma_g 1s)$, $u \equiv (\sigma_u^* 1s)$, and $\bar{g}$ indicates a spin down. The base functions of the product representations, ${}^4A_2 \times {}^1\Sigma_g^+$ and ${}^4A_2 \times {}^3\Sigma_u^+$ in the coupled-spin scheme are obtained by suitable antisymmetrization of the linear combination of the products of separate eigenstates with the Wigner coefficients $\mathcal{C}(S\Sigma J\,|\,m_s m_\sigma m)$. (Sm_s), (Σm_σ), and (Jm) are the chromia, molecule, and total electronic spin quantum numbers. The matrix elements of the total Coulomb interaction $C = \sum_{i<j} e^2/r_{ij}$, among the five electrons, are simply calculated in this coupled scheme. All the necessary elements of $\mathcal{X}$ may be deduced from the only nonvanishing element of C,

$$\langle {}^4A_2 \times {}^1\Sigma_g^+, J = \tfrac{3}{2} m \,|\, C \,|\, {}^4A_2 \times {}^3\Sigma_u^+, J = \tfrac{3}{2} m \rangle,$$

which is independent of m. If we only perform the orbital integrations, denoted by $\langle\,\rangle_0$, the corresponding spin Hamiltonian is shown to take the simple form

$$\langle \mathcal{X} \rangle_0 = \mathcal{H} \mathbf{S} \cdot \boldsymbol{\sigma}, \tag{4}$$

where $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$, $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ being the spin angular momenta of the H_2 electrons 1 and 2. Explicit calculation leads to

$$\mathcal{H} = -\frac{\sqrt{2}}{3} \sum_{w = \xi,\eta,\zeta} \langle wg \,|\, c \,|\, uw \rangle. \tag{5}$$

c represents the molecule-impurity two-electron Coulomb operator e^2/r. If we further neglect the integral overlap $S = \langle a \,|\, b \rangle$, where a and b stand for $1s$ atomic orbitals centered on the two protons a and b, $\mathcal{H}$ is simplified to

$$\mathcal{H} = -\frac{1}{3\sqrt{2}} \sum_{w = \xi,\eta,\zeta} \{\langle wa \,|\, c \,|\, aw \rangle - \langle wb \,|\, c \,|\, bw \rangle\}. \tag{6}$$

In Fig. 1, we illustrate the exchange of electrons attached to proton a and chromia ξ, for a particular flip-flop transition. The difference operator $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$, which yields the selection rule $\Delta\Sigma = 1$, induces the spin singlet-triplet transition ${}^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$. Moreover, the orbital average $\mathcal{H}$ is antisymmetric under permutation of the two protons a and b, so that exchange connects rotational states of different parities, and yields selection rule (1). In the ${}^1\Sigma_g^+$ ground state, the s (a) states correspond to even (odd) rotational para (ortho) states, while in the ${}^3\Sigma_u^+$ excited state they correspond to odd (even) rotational para (ortho) states. The selection rules associated with the X step are thus

$$\Delta L \text{ odd}, \quad s \leftrightarrow s, \quad a \leftrightarrow a, \qquad \Delta I = 0, \quad \Delta\Sigma = 1. \tag{7}$$

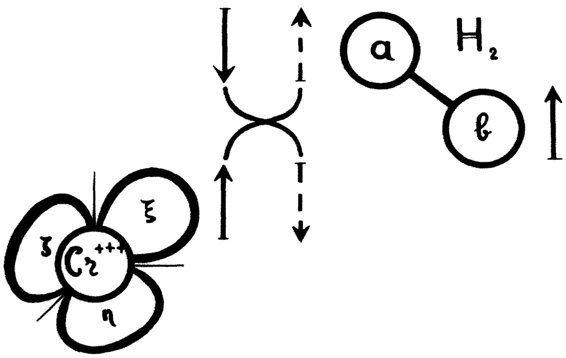

FIG. 1. One-particle exchange process between electrons a and ξ, corresponding to the flip-flop transition

$$|S = \tfrac{3}{2}, \Sigma = 0, m_s = \tfrac{3}{2}, m_\sigma = 0\rangle \rightarrow |S = \tfrac{3}{2}, \Sigma = 1, m_s = \tfrac{1}{2}, m_\sigma = 1\rangle.$$

The hyperfine step involves mainly a contact interaction between electronic and nuclear spins of the molecule. It is thus an intramolecular interaction of the usual form

$$\sum_{\substack{\alpha = 1,2 \\ \beta = a,b}} A_{\alpha\beta} \boldsymbol{\sigma}_\alpha \cdot \mathbf{i}_\beta,$$

where $\boldsymbol{\sigma}_\alpha$ and $\mathbf{i}_\beta$ represent the electronic and nuclear spin vectors. This contact interaction is at the origin of hyperfine structures in atomic or molecular spectra through its diagonal part, $\Delta\Sigma = \Delta I = 0$. Contradistinctly, here we are interested in singlet-triplet admixtures and we need only retain the nondiagonal part, $\Delta\Sigma = \Delta I = 1$, which is written as

$$\mathcal{Y}_c = \tfrac{1}{4} a \{\delta(\mathbf{r}_{a1}) - \delta(\mathbf{r}_{b1}) - \delta(\mathbf{r}_{a2}) + \delta(\mathbf{r}_{b2})\} \boldsymbol{\sigma} \cdot \mathbf{i}, \tag{8}$$

where $\mathbf{r}_{\beta\alpha} = \mathbf{r}_\alpha - \mathbf{r}_\beta$, $\mathbf{i} = \mathbf{i}_a - \mathbf{i}_b$, $\boldsymbol{\sigma} = \boldsymbol{\sigma}_1 - \boldsymbol{\sigma}_2$, and a is the usual hyperfine constant. The orbital integrations of $\mathcal{Y}_c$, between the ${}^1\Sigma_g^+$ and ${}^3\Sigma_u^+$ states, are nonvanishing as the orbital part of $\mathcal{Y}_c$ is antisymmetric for permutation of electrons 1 and 2, and nuclei a and b. We simply obtain

$$\langle \mathcal{Y}_c \rangle_0 = (a/2\pi\sqrt{2}) \boldsymbol{\sigma} \cdot \mathbf{i}. \tag{9}$$

This contact interaction, being intramolecular, involves no change in the rotational quantum number and may be evaluated in a frame attached to the molecular figure axis. The selection rules associated to the Y step are thus

$$\Delta L = 0, \quad s \leftrightarrow a, \quad \Delta\Sigma = \Delta I = 1. \tag{10}$$

The hyperfine interaction, yielding (2), completes the para↔ortho transitions. We do, however, emphasize that the exchange step is a time-dependent one (it contributes to the spectral density), whereas the hyperfine step admixes stationarily ground and excited electronic states. The symbolic picture of this two-step process is sketched in Fig. 2.

If we neglect energy differences between the intermediate states, and population differences in the impurity ground states, insertion of (4) and (9) in the conversion rate (3), for the $(p,L=0)\leftrightarrow(o,L=1)$ transition, leads to

$$\mathcal{P}_{p\to o}(XY)\sim\frac{a^2J_X(\omega_{op})}{8\pi^2\Delta_e^2}\sum_{\text{all }m}\left|\langle\Sigma=L=I=0,S=\tfrac{3}{2},m_s\,|\,\mathcal{O}\,|\,\Sigma=0,L=I=1,m_lm_i,S=\tfrac{3}{2},m_s'\rangle\right|^2, \tag{11}$$

where the operator $\mathcal{O}$ is defined by

$$\mathcal{O}=\mathcal{H}\boldsymbol{\sigma}\cdot\mathbf{S}\,|1\rangle\langle 1|\,\boldsymbol{\sigma}\cdot\mathbf{i}+(\text{H.c.}) \tag{12}$$

and $|1\rangle\langle 1|$ represents the projector on the ${}^3\Sigma_u^+$ $(\Sigma=1)$ molecular subspace. If we denote by k^2 the average of $KK^\dagger$ over the molecular orientations, the conversion probability (11) is calculated by means of some simple algebra[9] and found to be

$$\mathcal{P}_{p\to o}(XY)\sim(15/8\pi^2)(a^2k^2/\Delta_e^2)J_x(\omega_{op}). \tag{13}$$

Although we have restricted the discussion to the first excited electronic state $(b\,{}^3\Sigma_u^+)$, a similar argument may be extended by taking into account other excited states which satisfy selection rules (1) and (2) and give rise to additional contributions to the process.

It is of interest to compare the orders of magnitude of the XY and W processes which are written $(XY_c/\Delta_e)^2J_X(\omega_{op})$ and $Y_d^2J_W(\omega_{op})$. In order to compare the relative magnitude of J_X and J_W, we assume that the X and W time-dependent correlation functions are both exponentials with correlations times τ_X and τ_W. J_X and J_W are thus of Lorentzian shape. When the molecule approaches the impurity, the exchange integral increases (exponentially) more rapidly than Y_d $(\sim r^{-4})$. The X process is thus characterized by a shorter correlation time $\tau_X<\tau_W$. At room temperature, $\tau_X\approx10^{-13}$–10^{-14} s, $\tau_W\approx10^{-12}$–10^{-13} s. As the maximum efficiency for the o-p energy transfer occurs when $\tau=\omega_{op}^{-1}\approx10^{-13}$ s, J_X and J_W are of comparable magnitude at the o-p frequency ω_{op}. Then the efficiency ratio of these two processes is given by $(XY_c/\Delta_eY_d)^2$. Note that the contact ($1s$) hyperfine interaction is 100 times larger than the dipolar ($2p$) hyperfine interaction of a hydrogen atom. Since Y_d is the inhomogeneous part due to substrate spins, this difference is further enhanced. If one assumes a mean molecular-impurity distance of $r=3$ Å, our XY mechanism seems to be more efficient than the W mechanism if $X\gtrsim100$ cm^{-1}. This corresponds to the usual magnitude of exchange in solids. At lower temperature, $\tau_W>\tau_X\gtrsim\omega_{op}^{-1}$; thus $J_X>J_W$ and the difference between the XY and W processes is even larger. Therefore, we suggest this new reaction path as a possible interpretation of experimental conversion rates which are, at least, one (or two) order larger than Wigner theoretical ones.

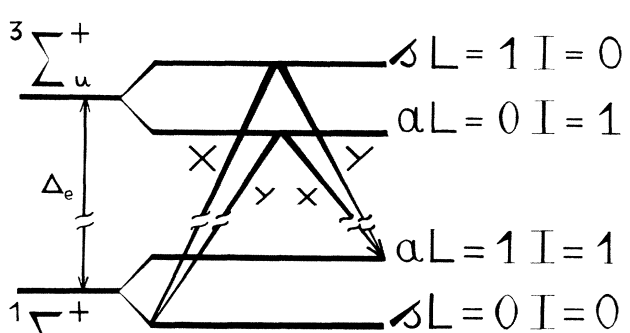

FIG. 2. The para → ortho $(L=0\to L=1)$ XY and YX transitions. Selection rules are, for X, $s\leftrightarrow s$ and $a\leftrightarrow a$; for Y, $s\leftrightarrow a$. ($\omega_{op}\approx10^2$ cm^{-1}, $\Delta_e\approx10^5$ cm^{-1}.)

If, during the catalyst pretreatment, the surface reduction is not completed, the magnetic impurities remain covered by an O$^-$ surface layer. Then the H_2 molecule will not approach the impurity closer than 4 or 5 Å. At this distance, the Wigner mechanism becomes negligible. Contradistinctly, our XY mechanism remains effective provided that the direct exchange of an electron between impurity and molecule is replaced by a superexchange one through the O$^-$ ligands. Moreover, such a long-range interaction converts, simultaneously, many molecules. It is interesting to remark that in Selwood's experiments the incomplete surface reduction of the catalyst gives rise to higher o-p rates than after complete reduction.[2,3]

We summarize with a few concluding remarks. (i) The virtual exchange of electrons between the impurity and the molecule admixes the singlet and triplet electronic states. Then it is the electronic spin of the molecule (instead of the impurity spin) that produces large inhomogeneous magnetic fields at the protons and induces the singlet-triplet nuclear transition. (ii) It is worth stressing some analogy with the exchange polarization of both the electronic charge and spin of a magnetic ion, in an antiferromagnetic compound, which allows the optical transitions otherwise both parity and spin forbidden.[13] (iii) Our model is equally valid for a magnetically dilute and dense substrate. In the latter case, energy may flow through the magnetic degrees of freedom of the catalyst.[6,8,10] Then the reaction rate should be very sensitive to volume, surface, and surface-molecule exchange interactions. (iv) The conversion rate relative to the W mechanism is strictly proportional to μ^2, where μ is the impurity magnetic moment. As the impurity orbitals contribute differently, because of their orientation, to the impurity-molecule exchange interaction the μ^2 law is not strictly obeyed by our XY mechanism. This could account for the observed fluctuation of $\sim100\%$, in the μ^2 law, in the rare-earth sesquioxides series.[5] (v) In this Letter, we have suggested that the

XY mechanism could be the leading one to convert H_2. If this process is confirmed by further experiments, fifty years of investigations in o-p-H_2 conversion would have to be reexamined.

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