

A Mechanism for the *para-ortho* Conversion of Hydrogen by Diamagnetic Substances

According to the Wigner theory (1) non-dissociative conversion of the hydrogen molecule between *para* and *ortho* states can occur only in the presence of an external inhomogeneous magnetic field. The mechanism responsible for the conversion reaction is profoundly fundamental, being related to the requirement for antisymmetry of the wave functions of the system. The inclusion in the Hamiltonian of a magnetic energy term which is uneven under interchange of coordinates allows nonzero matrix elements between spin eigenfunctions of different symmetry, and hence transitions between *J* even and *J* odd rotational states.

The Wigner theory interpreted the fine discoveries of Farkas and Sachsse (2) in which the *p-o* conversion reaction of hydrogen was catalyzed by paramagnetic gases and by paramagnetic ions in solution. However, in those experiments it was noticed that the conversion reaction could also be catalyzed by diamagnetic liquids such as water (H₂O), benzene (C₆H₆), methanol (CH₃OH), aniline (C₆H₅NH), cyclohexanol (C₆H₁₁OH), and carbon disulfide (CS₂). More accurate experiments by Farkas and Sandler (3) studied the conversion process for hydrogen dissolved in diamagnetic liquids which contained proton magnetic moments (such as H₂O) and liquids which did not (such as CS₂ and CCl₄). Although it was recognized that the proton magnetic moment could play a role in the *p-o* conversion, their results could not be explained without invoking some other source of inhomogeneous magnetic field.

In later absorption experiments (4-8), *p-o* conversion was observed as a surface phenomenon with diamagnetic solids such as germanium and silver. These experiments eliminated the possibility that the diamagnet-catalyzed conversion could be due to impurities: the suggestion was put forward that a "surface paramagnetism" of unknown origin was present in the diamagnetic materials. Inokuchi *et al.* (9) found that the *p-o* conversion process could be catalyzed by anthracene vapor under illumination. More recently Avouris *et al.* (10) have made direct observations of the conversion process by electron-energy-loss studies of H₂ on Ag surfaces, and have postulated a short-range magnetic interaction with the metal surface.

The set of diverse observations can be unified when it is noted that the *para-ortho* conversion reaction (and, indeed, any chemical reaction) takes place in the frame of reference of the molecule rather than in the laboratory frame of reference. The hydrogen molecules, which will have a velocity *v* due both to rotation and translation, will be moving through strong local electric fields (due to the electric multipole moments of the molecules which comprise the diamagnetic liquids, or due to the surface electric fields of the diamagnetic solids) and in their frame of reference will see a magnetic field of the order of vE/c^2 , where *c* is the velocity of light. The intensities of such relativistic magnetic fields will be small, about the same as that of the field due to the magnetic dipole moment of the proton; however, the field gradient, across the in-

ternuclear separation of the hydrogen molecule, will be large since the two protons will have opposite velocities caused by the rotation.

This role of the internal electric fields can be seen by comparing the rates of experimentally observed conversion reactions for hydrogen in simple liquids. Farkas and Sandler (3) found that the excess concentration of *p*-H dissolved in diamagnetic liquids decayed as $\exp(-ct)$, where the constant *c* was 62.8, 27.4, 6.4, and $4.6 \times 10^{-6} \text{ sec}^{-1}$, respectively, for H₂O, D₂O, CS₂, and CCl₄. The sequence is of interest since the waters are dipolar liquids, carbon disulfide is a quadrupolar liquid, and tetrachloromethane is octopolar.

For H₂O and D₂O at least part of the decay constant *c* can be ascribed to the inhomogeneous magnetic field arising from the magnetic dipole moments of the proton and deuteron. According to the Wigner theory, the rates should be proportional to the square of the nuclear moment, hence the rate for H₂O should be about 10.6 times that of D₂O were the fields of the nuclear dipoles the only mechanism causing the conversion reaction. The fact that the rate constants differ only by a factor of about two indicates that another mechanism must be operative.

Electrically, the two waters are very similar. They have almost identical dipole moments and the electric fields and relativistic magnetic fields seen by the hydrogen in solution should also be similar. Hence that part of the rate constant arising from the relativistic fields should be about the same for the two liquids, in distinction to the part arising from the nuclear magnetic dipoles which should differ by a factor of about 10.6. Expressing the rate constant for H₂O as $c = c_1 + 10.6c_2$, and that for D₂O as $c = c_1 + c_2$ an estimate gives $c_1 = 23.7 \times 10^{-6} \text{ sec}^{-1}$ and $c_2 = 3.7 \times 10^{-6} \text{ sec}^{-1}$. For H₂O, according to this estimate, the rate constant is comprised of a part of magnitude 23.7×10^{-6} due to the relativistic magnetic fields and a part 39.1×10^{-6} due to the proton

magnetic moment. Since CS₂ and CCl₄ have no proton magnetic moments present, their rate constants can be ascribed completely to the relativistic magnetic fields.

From the electric multipole moments of the liquids (11) it is possible to make estimates of the local electric fields. H₂O has a dipole moment 1.87×10^{-18} esu, CS₂ has a quadrupole moment 1.8×10^{-26} esu, and CCl₄ an octopole moment which is probably larger than that of CH₄, 1.8×10^{-34} esu. For the purpose of the estimate, the molecules can be simulated by arrays of point charges of the correct symmetry and spacing which produce the known multipole moments. The electric field at points near the centers of symmetry are then easily calculated. By this procedure the electric fields at a distance of 3 Å are estimated to be 4.5×10^9 V/m for H₂O and D₂O, 1.4×10^9 for CS₂, and 5.7×10^8 for CCl₄. It is in electric fields of these magnitudes that the hydrogen molecule rotates and translates.

The angular velocities of the different spin states of hydrogen are also easily obtained, and for the *J* = 2 state the tangential velocity of the proton is estimated to be about 4×10^3 m/sec. The relativistic magnetic field that will be seen can be estimated from vE/c^2 ; using the electric fields calculated above, the hydrogen molecule, at the 3 Å separation from the solvent molecule, will see magnetic fields of the order of 3 G for H₂O, 0.6 G for CS₂, and 0.25 G for CCl₄. The relative magnitudes of these magnetic fields are in accordance with the relative magnitudes of the rate constants for the *p*-*o* conversion (that is, 23.7, 6.4, and $4.6 \times 10^{-6} \text{ sec}^{-1}$).

The magnetic field due to the proton magnetic moment is of the same magnitude. Treating the proton as a point dipole of moment $5.05 \times 10^{-27} \text{ J/T}$, one proton produces a magnetic field of 1.3 G at a separation of 2 Å and 0.4 G at 3 Å. The field gradient of the proton magnetic moment will be larger than that of the relativistic magnetic field (which is proportional to the field, arising from the apparent change in direction of the field

across the hydrogen molecule).

The mechanism proposed here to explain p - o conversion of hydrogen by diamagnetic substances appears to agree with available experimental evidence, and explains a diverse body of experimental observation without invoking obscure and mysterious magnetic interactions. The mechanism is of great generality and will always be present when there is relative motion in an electric field. However, it need not be the only operative mechanism. For example, in the meticulous experiments of Van Caulwaert and Hall (11-13) on p - o conversion over alumina it was possible to completely eliminate the possibility of the reaction being caused by paramagnetic centers. These authors ascribed the reaction to the magnetic moment of exposed ^{27}Al nuclei; however (as was the case with the proton magnetic moment in water) the aluminum nuclei are more probably responsible for only a part of the conversion process, the balance being caused by the relative motion of hydrogen in the strong local electric fields of the alumina.

A variety of theories have been made available to explain p - o conversion under obscure circumstances. Nielsen and Dahler (15) have studied inhomogeneous magnetic fields which can occur during collisions of catalyst and reactant molecules. Ilicsa (16, 17) has studied the role of spin wave excitations on p - o conversion at magnetic surfaces, a theory elaborated in great detail by Petzinger and Scalapino (18), and also considered by Levy and Gallais (19). Levy (20) has studied phonon-assisted processes, and Bohnen and Pink (21) have suggested that the p - o conversion rate will vary greatly from site to site on a surface which sustains magnetic excitations. Again, it must be noted that many different mechanisms are possible, depending on the circumstances; however there are many clear cases (such as alumina and CS_2) where magnetic excitations simply do not exist.

The role of magnetic excitations and lo-

calized magnetic centers or clusters is of much more interest when the inverse side of the relativistic effect is considered. A molecule moving with velocity v in the presence of a magnetic field of intensity B will see a relativistic electric field of magnitude vB . This is a first-order relativistic effect (as compared to the vE/c^2 magnetic field, which is only of the second order), and allows a reactant molecule to experience very intense electric fields, where no static fields may exist, in the presence of a strong magnetic center. Such relativistic electric fields may explain the known efficacy of adding transition metals to catalysts (the transition metal ion or cluster would then comprise an active center in the process of catalysis), and may also explain the Hedvall effect (above the Curie temperature, where only short-range magnetic order can be sustained, the catalyst surface is more likely to show intense local magnetic centers).

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