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Anomalous Scalar Couplings in Trihydrides and Quantum Mechanical Exchange

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Anomalous NMR behavior has been observed in the ^{1}H spectrum of several classes of L_nMH_3 complex. This was first noted for $(\eta\text{-}C_5H_5)_2NbH_3$[1] and subsequently examined in more detail for the former complex[2] and cyclopentadienyl-substituted analogues[3,4] as well as $(\eta\text{-}C_5Me_5)RuLH_3$,[3,5] $[(\eta\text{-}C_5Me_5)Ir(PMe_3)H_3]^+$,[6] and $[(C_5H_5)IrLH_3]^+$.[7] In all published cases the three hydride protons exhibit the expected AB_2 pattern, but the apparent J_{AB} values show large temperature dependence and/or unprecedentedly high values, up to 1400 Hz![8]

Attempts to interpret these unusual observations have been couched in terms of "nonclassical" metal hydrides—structures involving a substantial degree of direct H-H bonding—either as equilibrating $M(\eta^2\text{-}H_2)H$ forms[3] or a novel $M(\eta^3\text{-}H_3)$ structure.[4,7] However, there are severe difficulties in any such explanation.

1. The observed couplings J_{AB} range up to nearly two orders of magnitude greater than for other proton pairs separated by two bonds. Even if some degree of direct bonding is supposed between the protons, no explanation has been offered for how this could lead to a coupling several times that of free H_2 (280 Hz, obtained by multiplying the observable value for HD by γ_H/γ_D).
2. The strong temperature dependence of J_{AB} is supposed[4,7] to result from changes in the position of the equilibrium between different structures; yet in all cases there is virtually no change in chemical shift with temperature, as would be expected for this model.
3. From the magnitude of J_{HH} the corresponding J_{HD} should be readily detectable; yet partially deuterium-exchanged samples exhibited no such coupling.[5,7,9] Such a reduction of an indirect spin-spin coupling[10] would require an extraordinary change in average conformation or in electronic structure upon isotope substitution. The near constancy of the chemical shifts, ν_A and ν_B, upon deuteration[5,7] suggests instead that there are at least two well-defined potential energy minima that are invariant to isotopic substitution.

In this communication we propose that these results are evidence of an entirely different mechanism of scalar coupling, quantum mechanical exchange. Exchange coupling is not a magnetic interaction, but rather a consequence of the spatial Hamiltonian when constrained by the symmetrization postulate.[11] Exchange coupling between nuclei is well-established[12-14] in ^{3}He and suspected in other low-temperature solids.[15,16] The requirement for exchange coupling is delocalization of quantum mechanically indistinguishable nuclei, such that two or more overlap. This delocalization is a property of the eigenstates and is distinct from thermally activated motion, such as chemical exchange.

The novelty of the present hypothesis is in proposing that exchange coupling of nuclei can appear in a liquid as an intramolecular scalar interaction between magnetically inequivalent sites. In all previous cases, such multiplet patterns have been interpreted as being due solely to the indirect mechanism.[10] The full scalar coupling is the sum of the indirect and exchange contributions $\mathcal{H}_J = \mathcal{H}_J^i + \mathcal{H}_J^e$. The exchange interactions may be classified by elements of the permutation group.[11,12] The possible such couplings in a three-spin system lead to a spin Hamiltonian

$$\mathcal{H}_J^e = J^{(2)}_{AB} I_A\cdot I_B + J^{(2)}_{BC} I_B\cdot I_C + J^{(2)}_{AC} I_A\cdot I_C + J^{(3)}(I_A\cdot I_B + I_B\cdot I_C + I_A\cdot I_C) \quad (1)$$

where I_A, I_B, and I_C are the spin operators for the three sites occupied by indistinguishable nuclei. The superscripts indicate pair (2) or cyclic (3) permutation.

The isotope substitution experiments[5,7-9] can now be interpreted in these terms. Since symmetrization does not restrict the possible states for different isotopes, the exchange coupling $J^e_{AB} \equiv J^{(2)}_{AB} + J^{(3)}$ will vanish between a proton and either a deuteron or a triton. This leaves only the usual J^i_{AB} contribution, which scales with the product of the magnetogyric ratios of the spins in question, whether distinguishable or not.

An exchange contribution is possible in principle between deuterons or between tritons if two or three are present. However, for pairs of nuclei that are predominantly localized near minima in their potential energy surface, overlap occurs mostly in the barrier region between minima and is expected to fall rapidly with increased mass. No experimental evidence that would indicate exchange coupling for the heavy hydrogen isotopes has been reported.

The above arguments identify the anomalously large couplings observed between protons in the AB_2 trihydrides as due to the exchange mechanism. The identification can be sharpened by considering the consequences of the two and three particle exchange mechanisms upon partial isotopic substitution. If a two particle exchange dominated, then the ABX species formed by isotopic substitution at one of the B sites would be expected to still show an anomalously large $J_{AB} \cong J^i_{AB} + J^{(2)}_{AB}$. This has been observed for $[(C_5H_5)IrLH_3]^+$ species with a single deuteron at a B site, where J_{AB} between the remaining protons increased by less than 10%.[8] If, on the other hand, cyclic permutation were the only appreciable exchange mechanism, then this species would show only the smaller J^i_{AB}, measurable independently (scaled by $\gamma_T/\gamma_H \cong 1.06$) as a proton-triton coupling.[9] Another recent observation allows us to conclude that the $J^{(3)}$ mechanism is negligible in these compounds; use of a chiral ligand in $[(C_5H_5)IrLH_3]^+$ gave an ABC spectrum with J_{BC}, the coupling between the formerly equivalent sites, to be 3.4 Hz and independent of temperature, while J_{AB} and J_{AC} are large, similar in value, and temperature dependent.[8]

Another anomalous feature of the trihydride couplings is their increase with temperature, although the chemical shift is nearly temperature independent. This result can be accommodated by the exchange mechanism if it is supposed that there is a ladder of eigenstates with spacings small enough that excited states are appreciably occupied in the range where J_{AB} is observed to increase with temperature and if tunnelling increases with energy even below the potential energy maximum. The observed coupling is the Boltzmann-weighted average over these levels. Such closely spaced levels are to be expected in a potential shallow enough to

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(9) The reduced J_{AB} between proton and deuteron may be obscured by rapid quadrupolar relaxation of the deuteron. However, had the reduction factor been only $\gamma_D/\gamma_H = 0.15$, then the coupling would have still been partially resolved, in contrast to the report[7] of single lines with FWHM $\cong$ 15 Hz. More recently J_{HT} has been observed in partially tritiated $[(C_5H_5)IrLH_3]^+$ to be anomalously reduced to only 25-30 Hz (Heinekey, D. M.; Zilm, K. W., personal communication, 1988).

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allow tunnelling, and so the picture is self-consistent. The collapse of the AB_2 pattern to a single line[5,7] is brought about in part by the increased tunneling as higher energy states are occupied before classical barrier crossing becomes important. The intermediate line shapes are not those predicted from the usual models of chemical exchange[17] in which a thermally activated barrier crossing (hopping) motionally averages the chemical shifts at a fixed coupling constant.

In summary, anomalous scalar couplings observed for metal trihydrides in solution are explicable as exchange couplings but not as indirect couplings. They do not indicate large electron density between protons but rather weak delocalization by pairwise proton tunnelling. The details of the potential and explication of its apparent variation with metal or ligands is a challenging problem.

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Note Added in Proof. A similar exchange mechanism has been proposed by Zilm et al. to explain these NMR observations. See the following communication in this issue.

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Proton-Proton Exchange Couplings in Transition-Metal Polyhydrides

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We have previously reported the synthesis and anomalous NMR properties of a series of cationic iridium trihydride complexes of the general formula $[(\eta\text{-}C_5H_5)Ir(L)H_3]BF_4$ (L = PMe_3, **1**; L = PPh_3, **2**; L = $AsPh_3$, **3**).[1] The low-temperature $^{1}H\{^{31}P\}$ spectra of these compounds in the hydride region are AB_2 patterns with extremely large, temperature-dependent and field-independent values of J_{AB}. Similar observations have been made by others on *neutral* trihydrides such as $(\eta\text{-}C_5Me_5)Ru(PR_3)H_3$[2] and $(\eta\text{-}C_5H_{5-n}R_n)_2NbH_3$[3] (R = $SiMe_3$; $n = 1, 2$). Attempts to interpret these observations in terms of a structural model have invoked either dihydrogen/hydride structures[2] or trihydrogen complexes[1,3] such as those suggested by Burdett and co-workers.[4] The magnitude of reported J_{AB} (up to 570 Hz) and the fact that these couplings are very sensitive to temperature is unprecedented in solution NMR. The exponential temperature dependence reported[1] previously can at face value be rationalized by an equilibrium between two species, with one having a small J_{HH} and the second having a large J_{HH}. However, the sheer magnitude of the required large J_{HH}'s cannot be readily accounted for by any of the factors giving rise to a normal J coupling[5] unless a very unusual electronic structure is invoked. This communication describes a compound which displays an even larger J_{AB} and a tritium labeling experiment whose result provides the key to the origin of these couplings.

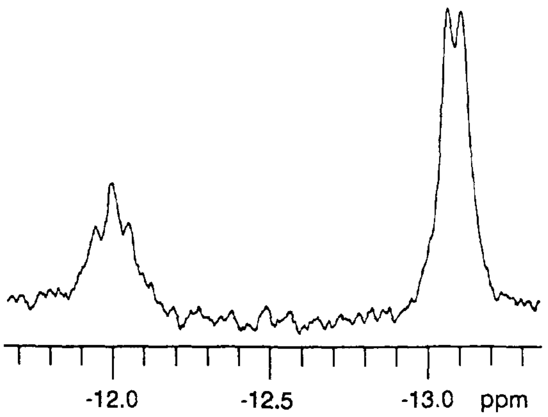

Figure 1. Tritium NMR spectrum of partially tritiated **3** recorded at 185 K on a 490 MHz proton instrument modified to operate at 522 MHz. Tritium incorporation was accomplished by a procedure analogous to the deuterium labeling procedure.[8]

As previously reported,[1] no H–D coupling has been observed in partially deuterated samples of complex **1**. Computer simulation of the ^{1}H line shape[6] confirms that the rapid quadrupolar relaxation of the ^{2}D nucleus ($T_1 \approx 25$ ms) at 193 K could preclude observation of the expected 19 Hz J_{HD} in **1** ($J_{HH} = 122$ Hz). The related complex **4** (L = MPTB[7]) has also been prepared. Since complex **4** gives an AB_2 spectrum at low temperature with J_{AB} values ranging from 1053 Hz (181 K) to 1397 Hz (196 K), it seemed almost certain that partial deuteration[8] would produce a resolvable H–D coupling. None was observed, and it seems unlikely that the ^{2}D T_1 could be sufficiently short to render the expected (150–200 Hz) J_{HD} unobservable unless the ^{2}D quadrupole coupling is also unusually large. In the absence of T_1 data, a definitive conclusion then cannot be drawn from this result. Because of these complications due to rapid deuterium relaxation and chemical exchange in the deuterium isotopomers, it was decided that conclusive results would only be obtained by using ^{3}T. The ^{3}T NMR of partially tritiated **3** at 185 K is shown in Figure 1. The $^{3}T_A$–$^{1}H_B$ and $^{3}T_B$–$^{1}H_A$ couplings are 29 and 24 Hz, respectively, rather than the ca. 530 Hz expected from the J_{HH} observed at this temperature.

This observation is quite remarkable and strongly suggests that the large J_{HH} couplings *are not magnetic in origin but are in fact exchange couplings*.[9-13] The model which best fits the NMR data for these trihydrides involves such couplings between the unique proton A and the two other protons B. In both NMR and ESR it has long been recognized that quantum mechanical tunneling[14-17] and exchange interactions[9-13] produce spectral features

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(7) MPTB = 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane. Complex **4** was prepared by methods analogous to those reported previously[1] for **1**-**3**.

(8) The cationic trihydrides readily incorporate D from D_2 (room temperature, 2 atm). This procedure is superior to the previously reported method involving exchange with D_2O.

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