J. Am. Chem. Soc. **1990**, *112*, 920-929

Quantum Mechanical Exchange of Hydrides in Solution: Proton-Proton Exchange Couplings in Transition-Metal Polyhydrides

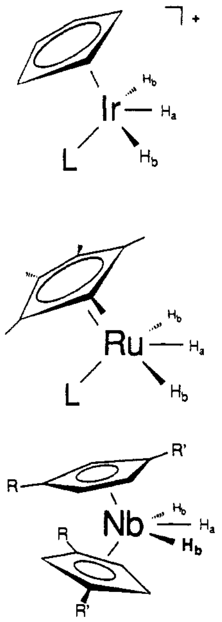
Kurt W. Zilm,*,[†] D. Michael Heinekey,* John M. Millar,[‡] Neil G. Payne, Steven P. Neshyba, James C. Duchamp, and Jolanta Szczyrba

Contribution from the Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06511. *Received January 18, 1989*

Abstract: Several groups have recently reported observation of unusually large apparent *J* couplings between protons in transition-metal trihydrides. The observation that these couplings are not present between ^1H and ^3T nuclei in partially tritiated isotopomers leads us to propose that these couplings are not magnetic in origin. They are in fact exchange couplings between protons in direct analogy to exchange couplings observed between electrons in radical pairs or between ^3He atoms in solid ^3He. This is a rather unexpected manifestation of quantum mechanical motion in these hydrides as it has been observed in solution at ambient temperatures. This paper presents in detail a simple theory that quantitatively predicts the size and pronounced temperature dependence of these couplings. The theory also explains the extreme secondary isotope effects observed in these couplings. It is proposed that these couplings should be observed in systems other than trihydrides. Furthermore these couplings are likely to be responsible for the appearance of some polyhydrides to be fluxional on the NMR time scale even at the lowest attainable temperatures in solution.

The proton NMR spectra of several transition-metal trihydrides have recently been noted to be characterized by extremely large scalar couplings.[1-4] In some instances these couplings have been observed to be over 1500 Hz. Attempts to rationalize the size of these couplings on the basis of structural features have been less than satisfactory given that the *J* coupling in molecular H_2 itself is only 280 Hz, as inferred from the NMR of HD.[5] Furthermore these couplings have an unprecedented temperature dependence. For some of the examples identified, the apparent *J* increases by over a factor of 15 when the temperature is raised 100 K.[3] This unusual behavior prompted a careful study of the temperature, field, and isotope dependence of these couplings. In this paper the collection of ^1H, ^2D, and ^3T NMR results for the compounds **1-14** are examined. The combination of these NMR data with structural details from solid-state ^1H NMR and neutron diffraction provides compelling evidence for the assertion that these large couplings are in fact due to quantum mechanical exchange.

Chart I



L = $AsPh_3$, **1** PCy_3, **6**
PPh_3, **2** $SbPh_3$, **7**
MTPB, **3** PMe_2Ph, **8**
PMe_3, **4** $P(OPh)_3$, **9**
P^iPr_3, **5**
P(H)(Ph)(n-decyl), **10**

L = P^iPr_3, **11**
PCy_3, **12**

R = R' = $SiMe_3$, **13**
R = H, R' = $SiMe_3$, **14**

Exchange couplings are well-known in ESR spectroscopy of many types of systems, including radical pairs and biradicals.[6-9] When the radicals in such systems are close enough to provide for significant overlap, the lowest singlet and triplet states are found to differ in energy due to the exchange interaction of the electrons. This energy difference between the singlet and triplet states can be observed as a pseudomagnetic coupling of the electron spins in the ESR spectrum if they are made magnetically inequivalent by their environment. In one sense the rate of exchange, i.e., the spectral splitting, can be viewed as the rate of mutual or correlated tunneling of the electrons between the two radical centers. Exchange couplings involving ^3He atoms in solid ^3He have been observed, albeit indirectly, in a variety of ways.[10] These couplings are responsible for the novel antiferromagnetic ordering of ^3He observed at cryogenic temperatures and for most of the unusual features of the NMR of ^3He.[10] In the case of ^3He, the wave function is rather delocalized as demonstrated by the large zero point vibrational amplitude of the ^3He atoms about their lattice sites. This delocalization permits pairs of ^3He atoms to exchange positions via the quantum mechanical exchange interaction. The compounds studied here are the first systems in which such an effect involving heavy particles has been directly observed as splittings in NMR spectra. Given that these couplings are mediated through vibrational motion, these results are quite surprising. This is especially so since the couplings are seen in the NMR spectra of molecules in solution at ambient temperatures. In what follows it will be seen that nearly all of the unusual

---

[†] 1988 Camille and Henry Dreyfus Teacher-Scholar.

[‡] Present address: Exxon Research and Engineering Corp., Annandale, NJ 08801.

(1) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303-2305.

(2) Arliguie, T.; Chaudret, B.; Devillers, J.; Poiblanc, R. *C. R. Acad. Sci., Ser. 2* **1987**, *305*, 1523-1526.

(3) Antinolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jolan, F.; Morris, R. H.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1210-1212.

(4) (a) Paciello, R. A.; Bercaw, J. E. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York; American Chemical Society: Washington, DC, 1986; INOR 82. (b) Paciello, R. A. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1987.

(5) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112-A117.

(6) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972.

(7) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford: London, 1959.

(8) Herring, C. In *Magnetism*; Rado, G., Suhl, H., Eds.; Academic: New York, 1968; Vol. IIB, pp 2-177.

(9) Anderson, P. W. In *Solid State Physics: Advances in Research Applications*; Seitz, F.; Turnbull, D., Eds.; Academic: New York, 1963; Vol. 14, pp 99-214.

0002-7863/90/1512-920$02.50/0

features of the NMR of these trihydrides follow from quantum mechanical exchange.

Theory

Alternative Models. In addition to quantum mechanical exchange, several other models have been considered that might explain the unusual NMR spectra of these transition-metal polyhydrides. At first the observation of these extremely large proton–proton *J* couplings in conjunction with the large apparent secondary isotope effects and temperature dependence seemed to plausibly be rationalized in terms of a dihydrogen/hydride $\rightleftharpoons$ trihydride equilibrium.[3] As more examples were synthesized and the couplings observed surpassed that in molecular hydrogen, this seemed unlikely. Explanation then seemed to hinge on the molecules possessing an electronic structure with rather low lying electronic excited states. However, when couplings exceeding 1500 Hz were observed, it seemed certain that none of the standard electron-mediated *J* coupling mechanisms[11] could be operative. An unusual feature of these compounds was the possibility that they could possess some η^2-dihydrogen complex character. With very close proton–proton contacts, the homonuclear dipolar interaction would be much larger than in normal polyhydrides. In dihydrogen complexes the proton shift anisotropy is also larger than typical.[12] Pople pointed out that in such a case a portion of the *J* coupling is due to a cross term between the shift anisotropy and the dipolar coupling.[13] This term can in fact be quite sizable on the scale of typical proton–proton *J* couplings, but it is still over a factor of 100 smaller than the large couplings observed.

Several models involving quantum mechanical motion of the protons have been investigated as the source of these couplings. Johnson pointed out that tunneling of a nucleus between two magnetically inequivalent sites would lead to the appearance of new spectral transitions.[14] Since it is known that in related η^2-dihydrogen complexes rotational tunneling occurs in the solid state at temperatures approaching 200 K,[15] it seemed reasonable to consider tunneling here. In the trihydrides **1–10** there are two equivalent protons H_B, and one unique proton H_A, which are bound to sites B and A, respectively. A typical model investigated along these lines involved having the unique proton H_A tunnel between two sites symmetrically disposed about the bisector of the H_B–H_B vector and in a plane containing all three protons. Such a model was motivated by the known existence in some trihydrides of a rapid isomerization between two isomeric η^2-dihydrogen hydrides.[16] *However, all such models failed to produce any splittings that were* independent of field strength and could therefore be mistaken for *J* couplings.

Rotational tunneling is also known to produce novel effects in the solid-state NMR spectra of methyl groups and other torsional oscillators.[17-22] Of particular significance is the recognition, again by Johnson,[23] that a free rotor or one tunneling at a high rate can display spectral features arising from mixing of different rotational levels by the dipolar interaction. This model, however, cannot account for the solution trihydride spectra in question as it predicts a particular field dependence that is not observed experimentally.

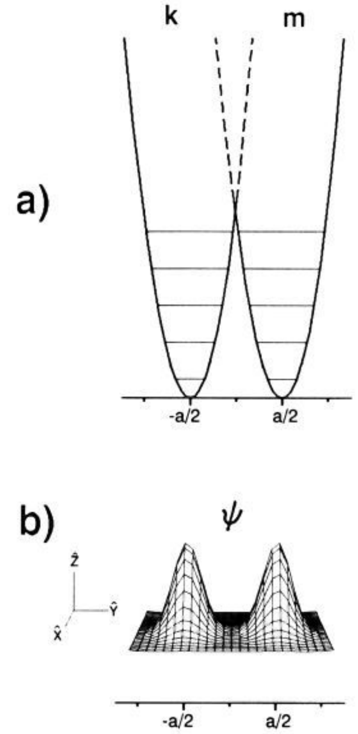


Figure 1. (a) A pair of harmonic potentials with $\nu_0 = 500$ cm^{-1} separated by $a = 1.65$ Å. This is a fair representation of the potential for motion along the equilibrium internuclear vector for the two-site exchange model. The harmonic oscillators for each well are drawn to scale. (b) The *x* and *y* parts of the 3D isotropic ground-state harmonic oscillator wave functions for the potential in (a). The classical barrier to exchange lies in the *xz* plane along $y = 0$.

Exchange Model. The one model considered that successfully accounts for these large couplings is quantum mechanical exchange. The theory of quantum exchange has been extensively studied as it pertains to the NMR and other magnetic properties of solid ^{3}He.[10,24-32] If a similar exchange mechanism is operative in these polyhydrides, this theory should at least be capable of producing order of magnitude estimates of these couplings and other pertinent experimental trends. The following discussion will focus on exchange between a single pair of particles even though three hydrogens are involved in exchange in the molecules being studied. The primary justification for this is the experimental observation that when the proton NMR spectra for the perprotio and $D_BH_BH_A$ isotopomers are compared, the large coupling in question between the unique H_A proton and the remaining H_B proton is observed to be contained in both systems. A more general treatment involving both pairwise and higher order permutations is also straightforward[10b,25,29] and leads to the same conclusions.

---

(10) (a) Abragam, A.; Goldman, M. *Nuclear Magnetism: Order and Disorder*; Clarendon Press: Oxford, UK, 1982. (b) Guyer, R. A.; Richardson, R. C.; Zane, L. I. *Rev. Mod. Phys.* **1971**, *43*, 532–600.

(11) Emsley, J. W.; Feeny, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, UK, 1965; Vol. 1, Chapter 3.

(12) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837–7839.

(13) Pople, J. *Mol. Phys.* **1958**, *1*, 216–222.

(14) (a) Johnson, C. S., Jr. *J. Magn. Reson.* **1987**, *73*, 545–547. (b) It should be noted that our **J** is equivalent to Johnson's Δ, and our Δ is his δ/2.

(15) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466–468.

(16) (a) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339–1440. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. J. *J. Am. Chem. Soc.* **1986**, *108*, 7000–7009. (c) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867. (d) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780–3782.

(17) (a) Johnson, C. S.; Mottley, C. *Chem. Phys. Lett.* **1973**, *22*, 430–432; (b) Ibid. *J. Phys. C* **1976**, *9*, 2789–2795.

(18) Watton, A.; Pratt, J. C.; Reynhardt, E. C. *J. Magn. Reson.* **1985**, *64*, 296–303.

(19) Clough, S.; McDonald, P. J.; Zelaya, F. O. *J. Phys. C* **1984**, *17*, 4413–4420.

(20) Powles, J. G.; Gutowsky, H. S. *J. Chem. Phys.* **1955**, *23*, 1692–1699.

(21) Stejskal, E. O.; Gutowsky, H. S. *J. Chem. Phys.* **1958**, *28*, 388–396.

(22) Haupt, J. *Phys. Lett.* **1972**, 389–390; *Z. Naturforsch. A* **1973**, *28*, 98–104.

(23) Johnson, C. S., Jr. *J. Chem. Phys.* **1973**, *59*, 623–627.

(24) Landesmann, A. *Ann. Phys. (Fr.)* **1973**, *8*, 53–79.

(25) (a) McMahan, A. K. *J. Low Temp. Phys.* **1972**, *8*, 115–158. (b) McMahan, A. K. *J. Low Temp. Phys.* **1972**, *8*, 159–169.

(26) Brandow, B. H. *Ann. Phys.* **1972**, *74*, 112–249.

(27) (a) Ostgaard, E. *J. Low. Temp. Phys.* **1972**, *7*, 471–489. (b) Goldstein, L. *Phys. Rev. A 8*, 2160–2172.

(28) Pollock, E. L.; Ceperly, D. M. *Phys. Rev. B* **1984**, *30*, 2555–2565.

(29) Thouless, D. *Proc. Phys. Soc., London* **1965**, *86*, 893–904.

(30) Guyer, R. A. *Phys. Rev. A* **1974**, *10*, 1785–1799.

(31) Guyer, R. A.; Mullin, W. J.; McMahan, A. K. *Phys. Rev. B* **1975**, *11*, 1045–1052.

(32) Guyer, R. A.; Zane, L. I. *Phys. Rev.* **1969**, *188*, 445–468.

In order to understand how quantum mechanical exchange produces the couplings and isotope effects observed in these NMR spectra, the lattice dynamics giving rise to the effect must first be discussed. As a starting point, consider two particles strongly localized in two distinct potential wells. For the trihydrides here these would be the binding sites for the H_A and H_B hydrides. If these hydrides are far enough apart so that they do not interact with one another, their vibrational motion can be treated independently. Assuming the potential wells are isotropic and harmonic, the single-particle ground-state orbital wave functions are Gaussians:

$$\Psi(r_i) = \left(\frac{A}{\pi}\right)^{3/4} e^{-Ar_i^2/2} \qquad A = \left(\frac{mk_i}{\hbar^2}\right)^{1/2} \tag{1}$$

which satisfy the single-particle Hamiltonians $\mathcal{H}_i$ about the sites i with vibrational force constants k_i. In the limit of infinite separation, i.e., zero overlap of the two particles, this basis will be a very good description of the ground state. Consider the situation depicted in Figure 1 where the hydrides are a distance a = 1.65 Å apart in sites where the harmonic oscillator fundamental frequency is 500 cm^{-1}. Even when placed this close, the single-particle wave functions overlap very little, as shown in Figure 1B where the x and y portion of the two wave functions is plotted for a fixed value of z.

Although two such particles must interact very little, the small but finite overlap of their wave functions gives rise to quantum mechanical exchange. A full treatment of this phenomenon is complex and the reader is referred to the works of Herring[8] and McMahan[25] for a complete exposition of the problem. The concepts important for this work can be developed by considering the two-particle Hamiltonian appropriate to the problem at hand:[7,24,32]

$$\mathcal{H}(1,2) = T(1) + T(2) + U(1) + U(2) + v(1,2) \tag{2}$$

The $T(i)$ here are the kinetic energy operators, $v(1,2)$ is the interparticle potential, and $U(i)$ are the double-well potentials experienced by the particles 1 and 2, which are essentially harmonic in the vicinity of the lattice sites k and m. As pointed out by Van Vleck,[7] the Hamiltonian is separable into two single-particle problems in the absence of $v(1,2)$. If the $U(i)$ are approximated by individual harmonic potentials at the two sites, a zeroth order solution would be the product wave function $k(1)m(2)$ in which particle 1 is in a state localized at site k, and particle 2 is localized at site m. The function $k(2)m(1)$ in which the particles have been permuted is also a perfectly good solution. If the particles are identical, these states are degenerate as they have the same total energies E. When the full Hamiltonian is considered, this degeneracy is lifted by the off-diagonal elements of $v(1,2)$ and the double-well character of the true potentials $U(1)$ and $U(2)$. The energy levels are then split by an amount $\pm\mathbf{J}$, which following Anderson[9] is approximately

$$\mathbf{J} = \langle k(1)m(2)|v(1,2)|k(2)m(1)\rangle - 2\langle k(1)|m(1)\rangle\langle m(2)|U(2)|k(2)\rangle \tag{3}$$

where the minus sign has been used to emphasize that the potential $U(i)$ is attractive while $v(1,2)$ is repulsive. With the degeneracy broken, the wave functions become the symmetrized and antisymmetrized combinations of the original states. One approximation that has been used[24,25,32] for the two lowest states of the Hamiltonian in eq 2 is

$$\Psi_A = \frac{1}{2^{1/2}}(k(1)m(2) - k(2)m(1))g_{12}$$

$$\Psi_S = \frac{1}{2^{1/2}}(k(1)m(2) + k(2)m(1))g_{12} \tag{4}$$

where $k(i)$ and $m(j)$ are Gaussians as in eq 1 for particles i and j centered at sites k and m. The pair correlation function g_{12} takes into account the effects of the interparticle potential $v(1,2)$. As pointed out by McMahan,[25] these coordinate eigenfunctions literally manifest the effects of an exchange process since they are not localized. A localized state such as $k(1)m(2)g_{12}$ is not an eigenstate when exchange is operative, but a superposition of delocalized wave functions is in eq 4. The delocalized states represent the net effect of the system passing back and forth between the localized states, which in this two-particle problem occurs at a rate of $-2\mathbf{J}/\hbar$. This quantum mechanical exchange effect can be viewed as a tunneling of the two particles between the respective sites, which is correlated because of $v(1,2)$. Besides correlating the motion of the particles, $v(1,2)$ reduces $\mathbf{J}$ by excluding from the available space tunneling paths in which the particles pass too close to one another. In a semiclassical sense $\mathbf{J}$ will be the probability per unit time that the two particles pass each other within the constraints of the potential $v(1,2)$ and end up having both passed from one potential well to the other.[31,32] If the particles possess spin, and experience different chemical shifts in the two sites, it is easily appreciated that quantum exchange will have an effect on the NMR spectrum.

Before turning to an explicit evaluation the effects of quantum exchange on NMR spectra and the calculation of $\mathbf{J}$, it is instructive to consider the situations where it will be important. Since the exchange interaction is an extremely small perturbation in the systems being considered, it will only be relevant when it connects localized states that are degenerate in energy.[29] Any two-particle system, regardless of the nature of the particles, will have this degeneracy lifted by $\mathbf{J}$ as long as the exchange of the particles does not change the total energy E. This is obviously the case when the two particles are identical and the two sites are chemically equivalent. This will also be true when the particles are identical, but the two sites are chemically inequivalent, i.e., the potential wells are of different depths as is the case for the H_A and H_B sites in the trihydrides studied here. Although the hydrides each have a change in their individual potential energies when they are exchanged between the two sites, the total energy E remains the same and quantum exchange will occur. Similar considerations arise in the case of exchange involving two distinguishable particles, a proton and a triton for example. If the two sites are chemically equivalent, the total energy of the two possible permutations will be degenerate. This degeneracy will again be lifted by the exchange interaction. Such a situation is encountered for ^4He impurities in a solid ^3He lattice where quantum exchange can provide a mechanism for impurity diffusion.[10b,32] However, in the trihydrides studied here, the exchange energy $\mathbf{J}$ is likely to come into play only when the A and B sites are inhabited by identical particles. Since the vibrational potentials will be slightly different in the inequivalent A and B sites, the exchange of a proton and a triton between these two sites leads to arrangements with different total energies because of the dependence of the vibrational energy levels on the particle masses. Unless the difference between these energies is smaller than or on the order of $\mathbf{J}$, the exchange process will largely be turned off. Therefore, in these particular polyhydrides replacement of a proton with a triton will quench quantum exchange due to this mass effect.

An explicit calculation of $\mathbf{J}$ usually proceeds by evaluating the difference of energy in the symmetric and antisymmetric states, $E_S - E_A = 2\mathbf{J}$, rather than by use of expressions as in eq 3. The surface integral expression used by Herring[8] and McMahan[25] has been found to be especially reliable for this purpose. This has been done by Landesmann[24] for a pair of particles in which the wave functions in eq 4 are used as approximations for the lowest symmetric and antisymmetric states. The interparticle potential is modeled by a hard-spheres interaction and is accounted for by a pair of correlation function g_{12}, which has the simple effect of zeroing the two-particle wave function in regions where the particles are closer than a characteristic distance λ to one another. The resulting expression for $\mathbf{J}$ is

$$\mathbf{J} = \frac{-\hbar A}{m}\sqrt{\frac{Aa^2}{2\pi}}\exp\left\{-\frac{A}{2}(a^2 + \lambda^2)\right\} \tag{5}$$

where a is the internuclear distance. This expression is valid as long as $A\lambda^2 \gg 1$, which in practice is easily fulfilled. Although derived for identical sites, this result will be taken as a good approximation to the case in which the two potential wells differ slightly in energy. In this case the most significant correction needed is to replace A in the exponential with the average of A_k and A_m for the k and m sites. Equation 5 is quite reasonable from the viewpoint of a semiclassical transition state theory description of the exchange process.[31-33] In this context, $\mathbf{J}$ should be proportional to the frequency that the particles approach the barrier, $\hbar A/m$, times the probability of both particles being at the top of the barrier.[31,32] Since the particles are strongly held in their respective potential wells, the most likely or minimum energy path has both particles pass over the barrier, i.e., in the xz plane midway between the two sites in Figure 1, on the edge of a circle of closest approach with diameter λ. The probability sought then will be proportional to the value of the two-particle wave function squared in this configuration, which is essentially the exponential term in eq 5 for $\mathbf{J}$.

A more useful equation for calculations is obtained by substituting $3/2\delta^2$ for A and converting to units of hertz:

$$\mathbf{J} = \frac{-3\hbar a}{8\pi m\delta^3}\left(\frac{3}{\pi}\right)^{1/2}\exp\left\{-\frac{3}{4}\frac{a^2+\lambda^2}{\delta^2}\right\} \tag{6}$$

where $\delta^2 = \langle x^2 + y^2 + z^2\rangle$ for the three-dimensional isotropic harmonic oscillator.[34] Equation 6 clearly identifies the delocalization of the individual particles δ^2 as a fundamental factor in determining the magnitude of the quantum-exchange rate. When either the particle mass or the vibrational frequency is decreased, the particles become more delocalized and δ^2 increases, which in turn increases $\mathbf{J}$. Thus, it can be appreciated that low vibrational force constants are just as important as small particle masses in producing a large quantum-exchange rate.

J and NMR Spectra. To see how $\mathbf{J}$ affects the spectrum of a pair of spins, products of the spin and orbital wave functions must be considered. In this situation the Pauli exclusion principle states that only the antisymmetric combinations exist in nature.[35] As a shorthand notation Ψ_A and Ψ_S will be denoted as A and S. The proper spin wave functions in terms of the usual spin $^1/_2$ product basis are

$$|1,1\rangle = |{+}{+}\rangle \quad |1,0\rangle = \frac{1}{2^{1/2}}(|{+}{-}\rangle + |{-}{+}\rangle)$$

$$|1,-1\rangle = |{-}{-}\rangle \quad |0,0\rangle = \frac{1}{2^{1/2}}(|{+}{-}\rangle - |{-}{+}\rangle) \tag{7}$$

where the first label refers to particle 1. The four antisymmetric products of the orbital and spin functions will be denoted as A(1,1), A(1,−1), A(1,0) and S(0,0). The magnetic portion of the Hamiltonian is taken to include only the chemical shift interaction. Taking ν_i to be the resonant frequency of a proton in a state i, i.e., $-\gamma H_0(1 - \sigma_i)/2\pi$, this can be written as

$$\mathcal{H}_z = I_{z1}(\nu_k\delta_{k,1} + \nu_m\delta_{m,1}) + I_{z2}(\nu_k\delta_{k,2} + \nu_m\delta_{m,2}) \tag{8}$$

where the Kronecker δ_{ij} equals 1 for particle j in site i and zero otherwise. Note that no magnetic scalar couplings have been included in $\mathcal{H}_z$. In the above basis the matrix for the full Hamiltonian $\mathcal{H}(1,2) + \mathcal{H}_z$ is

$$\begin{array}{cccc} \mathrm{A}(1,1) & \mathrm{A}(1,-1) & \mathrm{A}(1,0) & \mathrm{S}(0,0) \\ \end{array}$$
$$\begin{bmatrix} E_A + \Sigma & 0 & 0 & 0 \\ 0 & E_A - \Sigma & 0 & 0 \\ 0 & 0 & E_A & \Delta \\ 0 & 0 & \Delta & E_s \end{bmatrix} \tag{9}$$

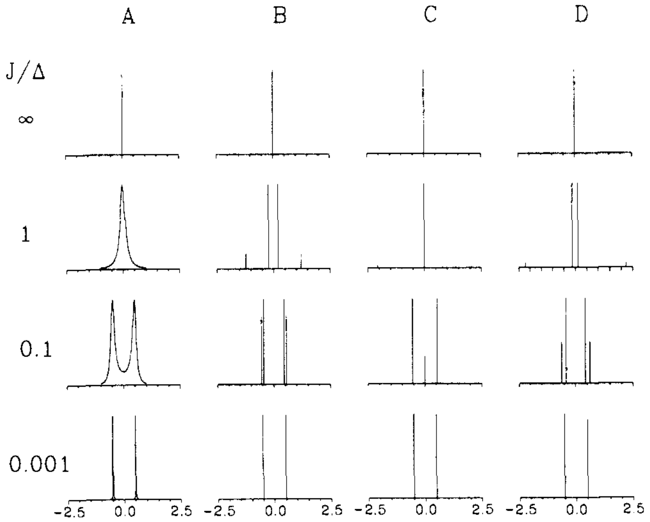


Figure 2. Comparison of spectra resulting from (A) classical two-site exchange, (B) quantum mechanical exchange, (C) exchange of a single particle between two wells by tunneling, and (D) quantum mechanical exchange of a proton/triton pair (only the proton spectrum is shown). These are depicted for several ratios of the rate of exchange to the chemical shift difference Δ. In these calculations the exchange rate is (A) the thermally activated rate, (B) **J**, (C) the tunneling frequency, (D) **J**.

where $\Sigma = (\nu_k + \nu_m)/2$; $\Delta = (\nu_k - \nu_m)/2$. It is instructive to compare this matrix to the Hamiltonian matrix constructed in the usual fashion for a pair of J-coupled spin $^1/_2$ nuclei with resonant frequencies ν_k and ν_m. In the same spin basis the matrix for the Hamiltonian $\mathcal{H}_z' = \nu_k I_{z1} + \nu_m I_{z2} + J I_1 \cdot I_2$ is

$$\begin{array}{cccc} (1,1) & (1,-1) & (1,0) & (0,0) \\ \end{array}$$
$$\begin{bmatrix} \Sigma + J/4 & 0 & 0 & 0 \\ 0 & -\Sigma + J/4 & 0 & 0 \\ 0 & 0 & J/4 & \Delta \\ 0 & 0 & \Delta & -3J/4 \end{bmatrix} \tag{10}$$

Any arbitrary constant energy can of course be subtracted off the diagonal of the secular equation for either matrix without affecting the energy differences, which are important for determining the spectrum. Subtracting the quantity $(E_S + 3E_A)/4$ from the diagonal in eq 9, and remembering that $E_S - E_A = 2\mathbf{J}$, results in a matrix with precisely the form as eq 10 if $-2\mathbf{J}$ is associated as the equivalent of J. Thus, the spectral transitions and intensities for an exchange-coupled pair of spin $^1/_2$ nuclei are exactly those of an AB spin system with the same chemical shifts and an effective scalar coupling J of $-2\mathbf{J}$. Since $\mathbf{J}$ is inherently a negative quantity, the effective coupling $-2\mathbf{J}$ is positive. If a magnetic scalar coupling J_m is also present, the total observed coupling $J = J_m - 2\mathbf{J}$. This result is of course not limited to the two-spin case. As noted by Dirac,[35b] the portion of the lattice Hamiltonian giving rise to any pairwise quantum mechanical exchange in a many fermion system is equivalent to an effective spin Hamiltonian of the form

$$-\tfrac{1}{2}\mathbf{J}_{ij} - 2\mathbf{J}_{ij}\mathbf{I}_i\cdot\mathbf{I}_j \tag{11}$$

Thus, in solving the NMR spectral problem, the effect of pairwise quantum exchange among several identical spin $^1/_2$ particles can generally be included by adding such coupling terms to the magnetic Hamiltonian.

It is interesting to note that if the Pauli principle had not been applied in the two-spin problem and the four additional wave functions of improper symmetry included in the calculation, the result is largely unchanged. The improper wave functions form another block with identical elements except for the interchange of E_A and E_S. Thus, the spectrum predicted would be identical but with an effective J of opposite sign. As long as the particles are identical, all matrix elements connecting the two 4 × 4 manifolds are exactly zero.

In Figure 2A are a series of two-site exchange spectra for various ratios of the classical exchange rate to Δ. Figure 2B compares these spectra to ones in which the same ratio of $|\mathbf{J}|$ to

---

[33] (a) Truhlar, D. G.; Garrett, B. C. *J. Chim. Phys.* **1987**, *84*, 365–369. (b) Hancock, G. C.; Truhlar, D. G. submitted for publication in *J. Chem. Phys.*

[34] Dunitz, J. D.; Schomaker, V.; Trueblood, K. N. *J. Phys. Chem.* **1988**, *92*, 856–867.

[35] (a) Baym, G. *Lectures on Quantum Mechanics*; Benjamin/Cummings: Reading, 1969; Chapter 18. (b) Dirac, P. A. M. *The Principles of Quantum Mechanics*; Oxford University: Oxford: Oxford, UK, 1958.

Δ is used. It will be shown later that $|\mathbf{J}|$ is expected to increase with rising temperature. As it does so the spectrum progresses toward a single line A_2 spectrum. This behavior is to be contrasted with the classical two-site exchange case in Figure 2A where the transitions broaden and coalesce before narrowing into a single peak.[36] As long as thermally activated exchange does not become rapid, increase in quantum mechanical exchange with temperature can lead to many of the spectral lines merging without any concomitant line broadening.[14]

When one of the protons in the trihydrides under consideration here is replaced by a triton, the quantum exchange is expected to be quenched due to the mass effect discussed earlier. Thus, the exchange coupling will disappear from the spectrum leaving behind only the magnetic J coupling to the heteronucleus. It should be noted that in a case where quantum exchange for different isotopes is not quenched by energetic considerations, the effect of quantum exchange on the NMR spectrum is somewhat different than in the homonuclear case. For two distinguishable spin $^1/_2$ particles such as a proton and a triton the Pauli exclusion principle no longer applies and the full 8 × 8 secular equation must be considered. The details of this calculation will not be presented here. It is sufficient to note for the present discussion that the spectrum of the nucleus being observed in this case is that predicted by Johnson[14] for a single-spin $^1/_2$ nucleus tunneling between two chemically shifted sites if this shift difference for the heteronucleus is vanishingly small. When this shift difference is finite, additional splittings occur that depend upon the chemical shift differences between the two sites for both nuclei. These later two cases are contrasted with classical exchange and homonuclear quantum exchange in Figure 2.

Temperature Dependence of J. Up to this point the treatment has only been concerned with quantum exchange in the ground vibrational state. A successful theory should also be able to reproduce the pronounced temperature dependence that has been observed experimentally for **J** (vide infra). This temperature dependence could arise from a temperature dependence of the vibrational potential, thermal population of higher lying vibrational states with enhanced rates of exchange, or some combination of both types of effects. McMahan[25] and Thouless[29] have pointed out in their treatments of exchange in solid ^{3}He that a rigorous calculation of the dependence of the exchange frequency on temperature must explicitly include a treatment of the temperature dependence of the lattice dynamics. For the molecules being considered here, however, the lattice dynamics are much simpler in many aspects than those in solid ^{3}He. Since the potential for the hydrides is intramolecular and determined by the molecular structure, it will largely be independent of temperature. Thermal population of higher vibrational states should then produce the dominant temperature effect. As the vibrational levels are widely spaced it will further be assumed that exchange process can be considered in each vibrational state separately.[29]

If the vibrational states were very long lived, distinct NMR spectra with increasing **J** would be observed for each higher vibrational state. However, under liquid-phase conditions the transition rate from one vibrational state to another[37] is expected to be on the order of 10^{10}–10^{12} s^{-1}. Because these transitions are so fast, the observed **J** will be a population weighted average over the thermally accessible states. This approximation will of course break down when vibrational states Ψ_n are populated with **J** values $\mathbf{J}_n$ that are larger than the vibrational transition rates. As long as the bulk of the population is in the ground vibrational state this is not a concern, as such large **J** values are only expected for vibrational levels close to the top of the barrier to classical thermally activated exchange. In this temperature regime the desired quantity then is

$$\mathbf{J}(T) = \sum_n P_n(T)\mathbf{J}_n \qquad (12)$$

where P_n is the fractional population of the nth vibrational state.

One could approach this problem by numerically calculating the $\mathbf{J}_n$ for a ladder of harmonic oscillator levels or for some other empirically chosen vibrational potential. Any realistic calculation[25b,28] is expected to be fairly computationally intensive as this is inherently a six-dimensional problem. For the purpose of gaining physical insight into the factors governing the temperature dependence of **J**, an approximate closed-form solution has been sought instead. Since the ground state **J** depends so strongly on the overlap of the two particles, it might be expected that $\mathbf{J}(T)$ will follow the temperature dependence of this overlap due to the increasing delocalization of the particles with rising temperature. This idea can be refined by using a potential energy integral[8,25,26] expression for **J**. McMahan[25a] has shown that Guyer and Zane's potential integral expression[32] in terms of their localized or home base wave functions is

$$\mathbf{J}_n = 2\langle\Psi_n(2,1)|\Delta U_k(1)|\Psi_n(1,2)\rangle + \frac{\hbar^2 Aa}{m}\langle\Psi_n(2,1)|\Psi_n(1,2)\rangle \qquad (13)$$

where the function $\Psi_n(1,2)$ and its permutation $\Psi_n(2,1)$ are home base functions analogous to $k(1)m(2)g_{12}$. A subscript n has been added here to denote the vibrational level. The difference potential $\Delta U_k(1)$ is that portion[32] of the full potential seen by particle 1 when localized in site k that provides for its attraction to the potential energy minimum at site m. Some simplification is gained by noting that $\Delta U_k(1)$ is just a function of the particle coordinates τ_1 and τ_2. Therefore, when eq 13 is inserted into eq 12, the sum and the integral can be interchanged. Making use of this fact, $\mathbf{J}(T)$ can be rewritten as

$$\mathbf{J}(T) = 2\int_{\tau_2}\int_{\tau_1} \Delta U_k(1)\cdot\vartheta(T)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 + \frac{\hbar^2 Aa}{m}\,\vartheta(T) \qquad (14)$$

where $\vartheta(T)$ is the population-weighted average over the vibrational states for the indicated overlap of the home base functions:

$$\vartheta(T) = \sum_n P_n(T)\cdot\Psi_n^*(2,1)\cdot\Psi_n(1,2) \qquad (15)$$

$\vartheta(T)$ has been calculated numerically by using a ladder of harmonic oscillator functions to form the $\Psi_n(i,j)$ for a system with physical parameters as depicted in Figure 1. This computed $\vartheta(T)$ is found to be very Gaussian. It is reproduced extremely accurately over the temperature range of interest by constructing a single temperature-dependent overlap function, $\Psi_T^*(1,2)\Psi_T(2,1)$, from Gaussians as in eq 1 but which have temperature-dependent widths. This temperature-dependent width is introduced by making the factor A a function of temperature by $A(T) = 3/[2\delta^2(T)]$ and choosing $\delta^2(T)$ to be the same as that for an isotropic three-dimensional harmonic oscillator. This $\delta^2(T)$ can easily be shown to be[34]

$$\delta^2(T) = \frac{3h}{8\pi^2 m\nu}\coth\left(\frac{h\nu}{2kT}\right) \qquad (16)$$

where ν is the harmonic oscillator fundamental frequency and m is the mass of the particle. In essence this approach is using the thermal ellipsoids[34] familiar from neutron diffraction or X-ray crystallography to approximate the required probability densities and their temperature dependence.

The problem of evaluating $\mathbf{J}(T)$ has now been reduced to finding **J** by using this temperature-dependent Gaussian to approximate the required overlap. This is quite easy as the ground-state expressions for **J** in solid ^{3}He have already been calculated using Gaussians for wave functions. In principle all of these expressions should be equivalent and one can simply replace the A parameter with $A(T)$ as above to produce an approximate expression for $\mathbf{J}(T)$. Since the surface integral results are expected to be the most reliable,[8,25] Landesmann's formula[24] as given in eq 6 will be used for $\mathbf{J}(T)$ by setting δ^2 equal to the expression in eq 16.

For $kT \gg h\nu$, $\delta^2(T)$ can be seen from eq 16 to be proportional to T/ν and thus **J** will have an exponential dependence on temperature. As the temperature is lowered, **J** will decrease and asymptotically approach the value dictated by zero point motion alone. In Figures 3 and 4 are computed plots of log **J** versus

---

(36) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University: Oxford, UK, 1961; Chapter 10.

(37) Pilling, M. J. Reaction Kinetics. *Oxford Chem. Ser.* **1975**, *No. 22.*

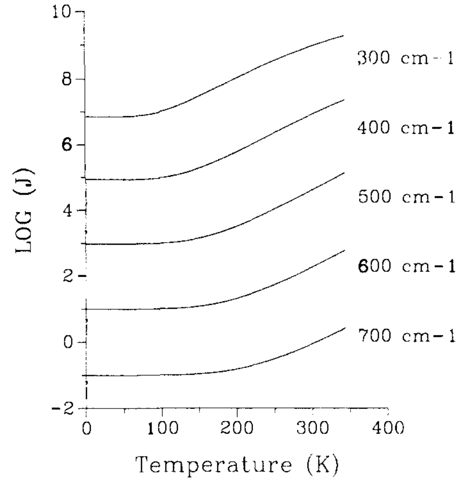


Figure 3. Plot of log $\mathbf{J}$ versus T for several values of ν. $\lambda = 1.0$ Å and $a = 1.5$ Å.

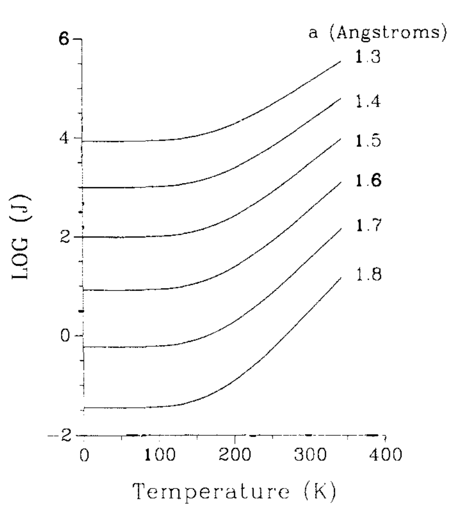


Figure 4. Plot of log $\mathbf{J}$ versus T for several equilibrium internuclear distances a. $\lambda = 1.0$ Å, $\nu = 550$ cm^{-1}.

temperature for a variety of distances a and frequencies ν with λ fixed at 1 Å. The plot in Figure 3 has a fixed at 1.50 Å and shows the variation in $\mathbf{J}$ versus T and ν. In this instance each additional 100-cm^{-1} decrease in ν results in 2 orders of magnitude change in $\mathbf{J}$. Figure 4 is a similar plot where ν has now been fixed at 550 cm^{-1} and a allowed to vary. Each 0.1-Å change in a results in an order of magnitude change in $\mathbf{J}$. These figures graphically underscore how extremely sensitive $\mathbf{J}$ is to these parameters.

The exchange frequency is also quite sensitive to the mass of the particles. The primary mass effect is the harmonic approximation comes from the dependence of δ^2 on mass. As $T \rightarrow 0$, $\delta^2 = 3\hbar/[2(mk_f)^{1/2}]$ where k_f is the appropriate vibration force constant. By use of a harmonic frequency $\nu = 500$ cm^{-1} and a distance $a = 1.65$ Å, $\mathbf{J}_{TT}$ for a pair of tritons is calculated to be over 4 orders of magnitude smaller than $\mathbf{J}_{HH}$ for a pair of protons in this low-temperature limit. At high temperature δ^2 becomes independent of the particle mass and is simply $3kT/k_f$. In this case the ratio $\mathbf{J}_{TT}/\mathbf{J}_{HH} = m_H/m_T$. This can be compared to the situation in solid helium where the helium atoms are even more delocalized and the mass dependence of $\mathbf{J}$ is much less severe. The ratio[32] of $\mathbf{J}$ for a ^{3}He/^{4}He pair to that for a ^{3}He/^{3}He pair even in the low-temperature limit is ~1/3.

Experimental Section

Details of the synthesis and ^{2}D incorporation for compounds **1**–**10** as well as their structural characterization and NMR parameters are contained in the companion paper in this issue.[38] Tritiation and ^{3}T NMR of **1** have been reported previously.[39] In brief, the proton NMR spectra, typically in CD$_2$Cl$_2$, at a variety of temperatures have been recorded for **1**–**10** at resonance frequencies of 250 and 500 MHz. The proton spectra of **2**–**4** deuterated at 30–50% have also been recorded over a similar range of temperatures. In addition, the ^{2}D NMR of **2**–**4** have been recorded on a spectrometer operating at 490 MHz for protons. ^{2}D T_1s for **3** and **4** have also been estimated from inversion recovery data. In all experiments temperature calibration is quite important due to the extreme temperature dependence of J. The spectrometers used were calibrated with a methanol standard.[40] The absolute temperature of the samples is estimated to be accurate to within ±1 K at all but the lowest temperatures attained. The temperature dependence of J in compounds **11**–**14** were taken from the tables in ref 3.[41]

The arrangements of the hydride protons in compound **2** were determined from the solid-state ^{1}H NMR line shape[39] at 77 K at a resonance frequency of 300.8 MHz on a home-built spectrometer described elsewhere.[42] To facilitate the recording of as clean a spectrum as possible, the phosphine and Cp ligands were perdeuterated[43] to a level of 98%. Spectra were recorded by using a dipolar echo sequence[44] with $\pi/2$ pulse times of 1.1 μs and a τ of 6 μs. The line shape was verified to be largely independent of τ.

Simulations of the solution proton NMR spectra recorded were done with the program PANIC on a Bruker WM-500. Proton line shapes of the partially deuterated isotopomers were calculated according to Pople[45] on an IBM PC/AT. Simulations of the solid-state proton NMR spectrum of **2** were done with a VAX 1180. Least-squares fitting of the temperature dependence of J according to eq 6 and 16 was also done on an IBM PC/AT and graphical output produced using the program PLOTIT.

Results

From analysis of the spectral data,[38] tables of J versus T have been compiled. Values for compounds **1**–**10** range from as low as 61 Hz to as large as 1565 Hz (see Table I). In all cases J has been observed to be independent of field strength within the accuracy of the temperature calibration. The chemical shifts for the two types of protons are also observed to be independent of both temperature and magnetic field strength. It should be remembered that the observed J is the sum of the magnetic coupling J_m and $-2\mathbf{J}$. For small J_m the theory predicts that J will inherently be positive since $\mathbf{J}$ is negative. Plots of the temperature dependence of J, superimposed upon a least-squares fit of the data using eq 6 and 16 to calculate $-2\mathbf{J}$ are shown in Figure 5. In all cases the fits are extremely good except at the lowest temperatures where the temperature calibration[40] is less accurate. In fitting this data, λ was fixed at 1 Å and the internuclear distance a and the vibrational frequency ν were allowed to float. Various estimates of J_m were also used. In all cases a unique fit was arrived at for a given J_m. When λ is changed from 1 Å the fits converge such that $a^2 + \lambda^2$ remains the same, and ν changes slightly to compensate for the preexponential dependence on a. Because of this interdependence, fits were not attempted in which all parameters were allowed to float. In light of the number of simplifications made in theory being applied, such sophistication in fitting the data would not be warranted. Table II contains the values of a and ν resulting from the fits shown in Figure 5. In all cases values of a around 1.6 Å and ν around 500 cm^{-1} were obtained. When the couplings are large the value of J_m chosen does not produce significantly different values for a or ν. On the other hand, when the observed couplings are smaller this correction is important. The nonzero J_m values quoted in Table II were chosen to give a and ν to be closer to the parameters determined for the compounds where exchange is dominant. In compounds **1**–**9** estimates of 0,

---

[38] Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.*, preceding article in this issue.

[39] Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 3088–3089.

[40] Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679–680.

[41] Chaudret, B., personal communication. The numbers used in this work were taken from tables provided by Prof. Chaudret rather than from the figures in ref 3.

[42] A 100-MHz spectrometer of nearly identical design is described in: Webb, G. G. Ph.D. Thesis, Yale University, 1988.

[43] Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 1954–1958.

[44] (a) Powles, J. G.; Mansfield, P. *Phys. Lett.* **1962**, *2*, 58–59. (b) Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. I. *Chem. Phys. Lett.* **1976**, 390–394.

[45] Pople, J. A. *Mol. Phys.* **1958**, *1*, 168–174.

Table I. J vs T for Compounds Studied[a,b]

cmpd	L	176 K	181 K	186 K	191 K	196 K	max. av error[c]
6	PCy_3	61	64	68	73	77	
		(61.$_1$)	(64.$_3$)	(68.$_0$)	(72.3)	(77.$_4$)	0.36
5	P^iPr_3	63.5	66.5	69	71.5	75	
		(63.$_9$)	(66.$_2$)	(68.$_8$)	(71.$_7$)	(75.$_0$)	0.38
4	PMe_3	96	106	114	122	135	
		(97.$_4$)	(104.$_8$)	(113.$_3$)	(123.$_2$)	(134.$_4$)	1.06
7	$SbPh_3$	147	158	171	180	196	
		(148.$_1$)	(157.$_7$)	(168.$_7$)	(181.$_4$)	(196.$_0$)	1.30
8	PMe_2Ph[d]	161	175	191	210	237	
		(159.$_9$)	(174.$_8$)	(192.$_0$)	(212.$_0$)	(235.$_2$)	1.49
2	PPh_3[e]	260	291	320	355	397	
		(255.$_4$)	(284.$_2$)	(317.$_7$)	(357.$_0$)	(403.$_2$)	4.12
9	$P(OPh)_3$	358	397	432	469	526	
		(360.$_5$)	(393.$_0$)	(430.$_6$)	(473.$_9$)	(524.$_0$)	3.3
1	$AsPh_3$[f]	376	419	460	512	570	
		(378.$_4$)	(416.$_3$)	(460.$_3$)	(511.$_4$)	(570.$_7$)	1.77
3	MTPB[g,h]	972	1119	1274	1425	1565	
		(998.$_4$)	(1113.$_7$)	(1248.$_2$)	(1405.$_7$)	(1589.$_7$)	22.0

[a] Unless otherwise specified, 500-MHz data, solvent CD_2CL_2, temperatures listed above. [b] Coupling constants in Hz. Calculated values from eq 5 and 6 using parameters contained in Table II are given in parentheses. Note that the J values reported are in theory all positive in sign. [c] Average deviation in Hz between observed and calculated J for worst case assumed magnetic J. [d] Measured at 250 MHz at 180, 183, 186, 191, and 196 K. [e] Data obtained at lower temperatures in $CHFCl_2/CD_2Cl_2$ mixture (4:1) at 490 MHz: 228 (171 K), 213 (167 K), 187 (160 K), 176 (157 K), 162 (153 K), and 151 Hz (150 K). [f] Measured at 490 MHz at 176, 180, 183, 186, and 189 K. [g] MTPB = 1-methyl-4-phospha-3,6,8-trioxabicyclo[2.2.2]octane. [h] Measured at 490 MHz.

Table II. H–H Distances and Vibrational Frequencies from J vs T Data

cmpd	L	magnetic J,[a] Hz	a, Å	ν, cm^{-1}
6	PCy_3	0	1.45	610.6
		25	1.62	537.9
5	P^iPr_3	0	1.34	674.6
		25	1.48	604.2
4	PMe_3	0	1.54	556.6
		25	1.65	513.3
7	$SbPh_3$	0	1.48	576.7
		25	1.54	551.4
8	PMe_2Ph	0	1.68	489.3
		25	1.62	511.8
2	PPh_3	0	1.66	488.6
		−25	1.62	503.1
9	$P(OPh)_3$	0	1.56	521.3
		25	1.59	511.3
1	$AsPh_3$	0	1.60	504.3
		25	1.62	494.8
3	MTPB	0	1.63	474.6
		25	1.64	472.3
12		0	1.78	466.3
		−25	1.64	513.4
11		0	1.70	492.1
		−25	1.59	533.6
14		0	1.43	678.5
		−25	1.14	847.1
13		0	1.42	671.8
		−25	1.22	780.6

[a] Note that a positive J_m adds to the inherently positive quantity $-2\mathbf{J}$ to give an overall J that is positive. A positive sign here indicates that the magnetic coupling augments the exchange coupling.

±10, and ±25 Hz were evaluated with none providing statistically superior fits. The calculated values of J for any of the compounds **1**–**9** differed only in the third figure after the fits had converged when using different J_m. The J values calculated from the $J_m = 0$ fit parameters are included Table I and are seen to differ from the experimental values by only 1–2%. For compounds **13** and **14** the observation that J goes to zero at low temperature requires J_m to be negative in sign.

A comparison of the experimental and calculated solid-state proton NMR of the hydrides in **2** is shown in Figure 6. Trial and error simulations result in the determination that the three protons form an isosceles triangle with a short side of 1.65 ± 0.05 Å and a long side of 2.2 ± 0.15 Å. Other symmetries produce spectra with very different characteristic shapes. These results are consistent with the neutron diffraction coordinates for **4** reported in the companion paper.[38] No attempts were made to correct the NMR distances for librational motion. Simulations in which rapid rotation or hopping of the three protons about an axis perpendicular to a plane containing all three failed to reproduce the observed spectra, indicating any such motion to be slow in comparison to the static dipolar couplings.

Table III. Root Mean Square Displacements[a] from Neutron Diffraction for **4**

atom	x	y	z	r	δ^b
H_A	0.156	0.218	0.307	0.219	
H_B	0.154	0.191	0.286	0.203	0.32
H_B'	0.169	0.220	0.291	0.221	

[a] From principal axes of thermal displacement tensors. Units are Å. $r = (xyz)^{1/3}$. [b] δ is the value of r from the isotropic harmonic model for $\mathbf{J}$ consistent with an H_A–H_B average distance of 1.686 Å. The observed J vs T curve is consistent with this distance if $\nu = 500$ cm^{-1} and the magnetic portion of $J = 32$ Hz, or if $\nu = 498.5$ cm^{-1} and the magnetic $J = 25$ Hz.

Table IV. J_{HH} vs T for H_2D and H_3 Isotopomers of Compound **2**

	J (H_2D)		J (H_3)		ratio	
T, K	exp[a]	calc[b]	exp	calc[c]	exp	calc
196	413	415	389	390	1.06$_2$	1.06$_5$
191	376	375	353	352	1.06$_5$	1.06$_5$
186	341	340	320	320	1.06$_5$	1.06$_4$
181	310	310	291	292	1.06$_5$	1.06$_4$
176	285	284	267	267	1.06$_7$	1.06$_4$

[a] J in units of Hz. [b] Calculated values using either $a = 1.555$ Å, $\nu = 515.7156$ cm^{-1}, $\lambda = 1.0$ Å or $a = 1.555$ Å, $\nu = 516.8908$ Å, $\lambda = 0.996$ Å. [c] Calculated by using $a = 1.555$ Å, $\nu = 516.8908$ Å, $\lambda = 1.0$ Å.

Some data on the vibrational amplitudes can be obtained from the neutron data[38] for **4**. This structure allows that the average H_A–H_B distance is 1.686 Å and the H_B–H_B distance is 2.665 Å. The root mean square amplitudes of the thermal vibrations along the principal axes of the thermal ellipsoids are given in Table III. The motion is anisotropic, with the largest displacement twice that of the smallest. For comparison to the J versus T data for **4** a fit was done with a fixed at 1.686 Å. The δ value obtained from the resulting ν value is seen to be in fair agreement with the root mean square r obtained from the neutron diffraction data (Table III).

In addition to the marked size and temperature dependence of the observed J couplings, the partially deuterated isotopomers show very large apparent secondary isotope effects. Replacement

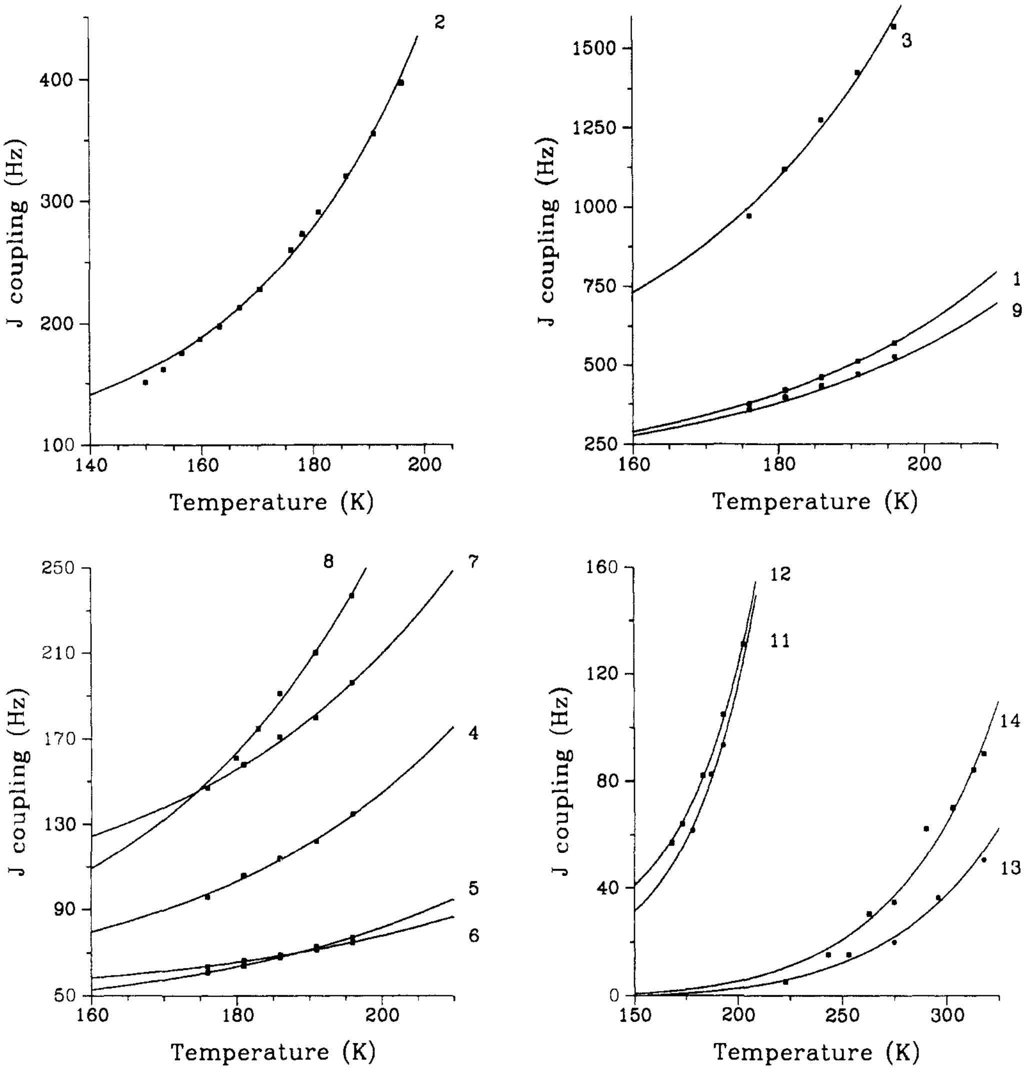


Figure 5. Comparison of the calculated fits to the experimental J versus T data for compounds **1–9** and **11–14**. Data for compounds **11–14** were taken from ref 3.

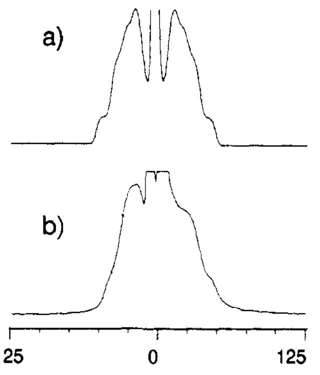


Figure 6. Comparison of the (a) calculated and (b) experimental solid-state proton NMR spectra for **2**. Much of the intensity at the carrier frequency comes from the residual protons remaining in the Cp and phosphine ligands.

of one of the protons H_B by a deuteron in **2** results in an AB spectrum for the remaining pair of protons with a J about 6% larger. Table IV gives the J measured in the H_3 and H_2D isotopomers in the same sample versus temperature. This result is simulated by either decreasing λ in the H_2D isotopomer from 1 to 0.996 Å or by decreasing the vibrational frequency ν by ca. 1 cm^{-1}.

The deuterium T_1 for compound **4** has previously been reported as 25 ms at 183 K.[1] A T_1 value for compound **3** has been measured now as well and is approximately 60 ms. These numbers must be taken as quite rough due to the poor solubility of these compounds at low temperature, which results in rather poor signal to noise in the ^{2}D NMR. The deuterium spectra for both of these compounds display broad resonances in a ratio of 2:1. No preference for ^{2}D to occupy either site in these trihydrides has been observed. Since the ^{2}D spectra are the result of the many different multiplets from the various isotopomers present at 30–50% deuteration, the presence or lack of HD coupling is not positively determined from the ^{2}D NMR. On the other hand, the proton spectra of the various isotopomers are more cleanly separated. In no case has any HD coupling been observed in these spectra. For compound **4** the short T_1, the uncertainty in T_1, and the complications of chemical exchange make it difficult to make any convincing conclusions on this basis. If the J_{HH} for **4** at this temperature were magnetic, the expected J_{HD} would be 19 Hz. Using this J value with the T_1 of 25 ms in simulations[45] produces a proton spectrum that is a broadened triplet in which the outer lines are half as intense as the inner line. With a T_1 of 12.5 ms the fine structure is completely collapsed and a single line with a fwhm of 19 Hz is calculated. Although the experimental proton spectra have narrower line widths (13 Hz fwhm), this cannot be unambiguously interpreted as evidence for lack of an HD coupling. If there were no HD coupling, the line width would not be expected to be much different from the perprotio line width of 2 Hz at this temperature. Without another verifiable explanation for this large increase in line width upon deuteration, little can be confidently inferred from this result alone. In the case of compound **3**, however, the much longer T_1 and the line width of 8 Hz cannot be easily rationalized if the J_{HH} were magnetic. For compound

3 it is quite clear from these data that no large HD couplings are present as they would have produced well-resolved splittings in the ^1H NMR spectrum.

The tritium NMR spectrum of **1** has been previously reported.[39] The lines are broad, ca. 10 Hz, and display resolved HT couplings. When the A site is tritiated this coupling is 29 Hz. For tritium in the B site the coupling becomes 24 Hz. These results then are the most positive proof that the apparent couplings have a pronounced dependence upon the mass of the isotope of hydrogen and are not magnetic in origin. If these couplings were magnetic, a coupling of ca. 530 Hz should have been observed instead.

Discussion

As just stated the small HT couplings observed in the ^3T NMR of compound **1** provide convincing positive proof that the large apparent J_{HH} couplings observed are not the usual magnetic scalar couplings. The absence of any resolvable HD coupling and the observation of the very small HT couplings are of course a direct consequence of the exchange model. When a proton is replaced by a triton or deuteron the quantum exchange is quenched by the mass effect discussed earlier. The absence of exchange coupling between the B and C sites in the ABC spectrum of the unsymmetrically substituted species **10** is also predicted by the theory because of the much larger H_B–H_C distance.

The fits of the temperature dependence of J in compounds **1–14** demonstrate that the model proposed here to explain the temperature dependence of these nonmagnetic couplings is basically sound and fairly quantitative. If the hard-spheres potential is a reasonable assumption, the fits would indicate that the λ required must be close to 1 Å if the a values are to agree with the known structural parameters from solid-state NMR[39] and neutron diffraction.[38] As mentioned before the fits basically determine $a^2 + \lambda^2$ independently of the frequency ν. Since many of these trihydrides are cationic, it is reasonable to ask whether the exchange involves protons or hydrogen atoms. The value of λ used is consistent with the particles undergoing exchange being hydrogen atoms. Typical λ values for hydrogen used in molecular mechanics calculations are usually larger,[46] ca. 1.3–1.4 Å. However, in such calculations a λ of 1 Å is used when hydrogen is attached to a heteroatom.[46] Thus, a 1-Å λ is reasonable in these systems given that the hydrides are bonded to transition metals. While this observation is self-consistent with the model proposed, it should only be taken as suggesting that the exchanging species are describable as hydrogen atoms.

The interproton distances in Table II resulting from the fits of J versus T are in reasonable agreement with the numbers obtained by solid-state NMR for **2** and neutron diffraction for **4**.[38] The variations in a again should not be taken too literally as they depend upon the λ and J_m values chosen as demonstrated in Table II. Depending upon the electron-withdrawing ability of the transition metal and its other associated ligands, λ could vary significantly. More importantly, the pairwise potential may not always be accurately represented by a hard-spheres approximation. It is well-known that in other transition-metal polyhydrides equilibria between dihydride and η^2-dihydrogen forms are common.[16] This observation suggests that there may actually be attractive terms in the pairwise potential. In general then the potential that determines the exchange frequency may be quite complex. Thus it is difficult to unambiguously interpret the variations in the distances a derived from the current treatment.

Of the simplifications used in the exchange model one of the least physical is the assumption of an isotropic harmonic potential for each hydride. A more realistic model would at least allow for the M–H stretch to be several times stiffer than the wag.[47] In such a model the M–H wag will have to be somewhat softer to compensate for the stiffening of the stretch if the same value of **J** is to be obtained. In other words, the increase in localization of the hydrides as the stretch is stiffened would have to be offset by more delocalization via a softer wagging motion. This goes along with the semiclassical picture of exchange as this is the motion most important for moving the two hydrides toward one another. Given the sensitivity of **J** to ν, the ν values reported should also not be taken too literally. While they are reasonable for M–H wags and undoubtedly close, the ν values determined indirectly here have most certainly compensated for the various approximations used in the model presented. The temperature dependence of **J** is to be viewed as a consequence of the temperature dependence of δ^2. In the isotropic harmonic approximation ν then is the parameter that determines this temperature dependence. Since the model uses an isotropic harmonic oscillator, the ν value must produce a thermal sphere that approximates the actual anisotropic and anharmonic motion. The comparison made between the neutron data and NMR data in Table III supports this view.

Even in light of the above critical assessment of the parameters resulting from the fits of J versus T, it is clear that the simple theory proposed for the temperature dependence of J is qualitatively correct. The parameters determined are physically reasonable and the overall temperature dependence for 13 compounds fitted rather accurately. Although the isotropic harmonic potential used here might be expected to be too simple a model, it does surprisingly well. In addition to agreeing with the temperature dependence of J, the neutron structure, and the neutron thermal parameters, the simple harmonic model parameters provide for a potential energy surface consistent with the onset of classical thermally activated exchange. In all of the cases studied here, as the temperature is increased the spectral transitions eventually do broaden and the lines coalesce before **J** itself can become large enough to collapse the spectrum. Clearly this is the result of thermally activated exchange coming into play in addition to quantum mechanical exchange.[17,19] A rough estimate of the barrier to classical exchange is provided by the 13.2 kcal energy difference between ground state and the crossing point of the two single-particle potentials drawn in Figure 1 for $a = 1.65$ Å and $\nu = 500$ cm^{-1}. The crossing point will on the one hand somewhat underestimate the barrier to thermally activated exchange as both particles cannot pass over the saddle point simultaneously, nor should both particles inhabit the same well. On the other hand, the potential is likely to be considerably lowered by anharmonicity corrections near the barrier. Apparently the latter factor is the more important as the barrier to thermal exchange is observed to be of the order of 10 kcal mol^{-1} in compounds such as **1–10** as well as in related systems.[48]

Many other observations can also be explained with this exchange coupling model. Substitution of a deuterium for one of the B-site protons leads to an increase of 6% in the **J** of the remaining H_A–H_B pair. There are two ways of rationalizing this behavior. The most plausible is to note that the incorporation of a ^2D nucleus in this site can decrease the vibrational frequencies of the adjacent sites, a secondary isotope effect. If this decrease is only 1 cm^{-1}, the change in J is fully accounted for. Another possibility is that the ^2D will be somewhat more localized than a proton in the same site. This will allow the neighboring proton to become more delocalized as there is more available space for it to occupy. The extra delocalization can be modeled by reducing λ to an effective value that permits this extra delocalization. If λ is reduced from 1 to 0.996 Å the secondary isotope effect on J is again reproduced.

The increase of J accompanying a decrease in ν as predicted by the theory also qualitatively explains much of the variation in **J** from compound to compound. In compounds **1–10** J is observed to go up as the coordinating ligands become less basic. This in turn lowers the M–H stretching frequency and presumably the M–H wag, thereby increasing J. The unusually large isotope effects on the chemical shifts are probably related to the exchange process only insofar as both effects are enhanced by low vibrational frequencies.[49] The data base for such isotope shifts in polyhydrides

---

(46) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S., Jr.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765–784.

(47) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128.

(48) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502–3507.

is quite small. It is, however, very plausible that the significantly lower vibrational frequencies of transition-metal hydrides in comparison to organic compounds are responsible for these large secondary isotopic shifts.[49] A firm interpretation of this result awaits a more complete study of isotopic chemical shifts in metal hydrides.

The observation of unequal HT couplings in the $H_BT_AH_B$ and $H_BH_AT_B$ isotopomers of **1** is also quite striking. Although it has been shown here that quantum mechanical exchange can occur in theory between a proton and a triton, it is unlikely that this is responsible for the splittings observed here. Since the A and B sites are chemically inequivalent, the difference in energy between the two positional isomers should be several orders of magnitude greater than any reasonable **J**. Therefore the quantum exchange is expected to be quenched. However the 25 and 29 Hz values reported are unusually large J_m values for polyhydrides. Such a large isotopic effect on a magnetic scalar coupling is also unprecedented to our knowledge and these observations merit further study.

Although not treated explicitly here, another feature of the NMR spectra of these compounds should be mentioned. In these and other related polyhydrides, the line widths observed are very often significantly wider than would be expected from T_1s if extreme narrowing is assumed.[50] The relaxation behavior of these systems may also be affected by quantum exchange.[10,51-53] Careful consideration of the effects of quantum mechanical exchange on T_1s and T_2s in these systems would be helpful. This may be important in the quantitative interpretation of proton T_1s for these systems, which has been attempted[3] along the lines of the T_1 method used to characterize η^2-dihydrogen transition-metal complexes.[50]

Conclusions

The unusual NMR properties of the transition-metal trihydrides **1–14** have been largely explained by a simple theory involving pairwise quantum mechanical exchange of the hydrides. The values of the parameters used in this model are in good quantitative agreement with what is known structurally about these compounds. In addition the primary and secondary isotope dependences of the couplings are explained. Although a purely quantum mechanical effect, this exchange process can be viewed semiclassically as a physical exchange of two particles between two sites. Further refinement of the model will require a more realistic treatment of the vibrational and interparticle potentials. As a first step, allowing the vibration to be anisotropic and anharmonic will go a long way toward producing a more accurate theoretical description of this exchange phenomenon. Accurate vibrational data would be quite helpful in this development.

While the model used at face value treats the hydrides here as essentially normal terminal hydrides, it is not proof positive that there are no bonding interactions between these hydrides. It is just not necessary to invoke bonding interactions. Interpretation of these results in terms of the bonding will probably require a much better understanding of the potentials involved. This will also be helpful in providing a more quantitative accounting of the unusual isotope effects upon chemical shifts and the difference in HT couplings between positional isomers.

These compounds should serve as ideal systems for further study of quantum mechanical exchange. The availability of three magnetic isotopes and a variety of structures will be useful in understanding higher order correlations. These polyhydrides should also be good systems for testing of the semiclassical theoretical approaches to tunneling that have found much use in treating chemical reaction dynamics.[33] In addition, they should prove to be good experimental systems in which the transition from quantum mechanical to classical motion[17,19] can be studied.

The model used to explain the NMR properties of these trihydrides is in no way restricted to trihydrides. It is expected that such exchange couplings should be observable in dihydrides and other polyhydrides. The observation that some polyhydrides seem to be fluxional in solution at all experimentally attainable temperatures may not always be due to facile thermally activated exchange as currently assumed.[54] Instead it may be the case that many such systems may possess very large exchange couplings and study of such systems might be facilitated by tritium NMR. Evaluation of suitable candidates for study may be made using the theory presented here to estimate **J** in conjunction with structural data. If anything is unique about the class of trihydrides examined herein, it may be that the structure and vibrational potentials just happen to be such that the **J** values are not too large nor too small to be observed given the available chemical shift dispersion. While proton–proton contacts in organic molecules can be as close as in these trihydrides, the theory predicts that the vibrational frequencies in organic systems are too high to permit observation of these quantum mechanical exchange effects at ambient temperatures.

In conclusion the observation of quantum mechanical exchange in these systems is a fascinating example of how quantum mechanical motion of nuclei can produce novel effects in NMR spectra. The fact that the splittings observed are only the order of tens to thousands of hertz and the NMR lines still only a few hertz wide shows that this relative nuclear motion remains coherent on an extremely long time scale even though the effect is mediated via the vibrational potentials. That the effect occurs in solution at ambient temperatures dramatically points out that heavy-particle quantum mechanical exchange effects should not be considered as only important at cryogenic temperatures. Heavy-particle tunneling[55-57] has been invoked in transport in biological systems[55,56] and on metal surfaces,[55,56] and in organic reaction mechanisms.[55,56] It will be interesting in the future to see if quantum mechanical exchange effects will now be identified as important in these other areas of chemistry.

Acknowledgment. K.W.Z. would like to acknowledge partial support of this work by a grant from the Exxon Educational Foundation and the National Science Foundation under Grant CHE-8517584. J.M.M. acknowledges support by an Exxon postdoctoral fellowship during a portion of this work. J.C.D. acknowledges support of a graduate fellowship from the Heyl Foundation. D.M.H. acknowledges support from the National Science Foundation under Grant CHE-8814191. We acknowledge stimulating discussions with J. M. McBride and J. W. Faller during the course of this work.

---

(49) (a) Jameson, C. J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1988**, *17*, Chapter 1. (b) Jameson, C. J.; Olsten, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 2497–2503.

(50) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.

(51) Clough, S. *J. Phys. C* **1971**, *4*, 2180–2190.

(52) Clough, S.; Mulady, B. J. *Solid State Phys.* **1972**, *5*, 2834–2844.

(53) Emid, S.; Wind, R. A. *Chem. Phys. Lett.* **1975**, *33*, 269–274.

(54) Jesson, J. P. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 75.

(55) Jortner, J.; Pullman, B., Eds. *Tunneling*; Reidel: Dordrecht, The Netherlands, 1986.

(56) Heidemann, A., Magerl, A., Prager, M., Richter, D., Springer, T., Eds. *Quantum Aspects of Molecular Motions in Solids*; Springer-Verlag: Berlin, 1987.

(57) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.