

## $^2\text{H}$ NMR Theory of Transition Metal Dihydrides: Coherent and Incoherent Quantum Dynamics

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In this paper a simple phenomenological description of the effects of coherent quantum and incoherent mutual exchange of two deuteron nuclei in solid state transition metal complexes on their  $^2\text{H}$  NMR spectra is given. This description is based on the quantum-mechanical density matrix formalism developed by Alexander and Binsch. Only the nuclear spin system is treated quantum mechanically. The quantum exchange interaction in NMR is included in the nuclear spin Hamiltonian, and the interaction with the surrounding bath and incoherent exchange processes are treated as phenomenological rate processes described by rate constants. The incoherent exchange corresponds formally to  $180^\circ$  rotations or jumps of the D–D vector around an axis perpendicular to this vector and averages the different quadrupole splitting of the two deuterons. In principle the dideuteron pair will exist in several rovibrational states. However, if the interconversion among these states is fast, the dideuteron exchange can be described by an average exchange coupling or tunnel frequency  $X_{12}$  and a single average rate constant  $k_{12}$  of the incoherent exchange. It is shown that the incoherent exchange gives rise to a relaxation of rate  $-2k_{12}$  between coherences created between states of different symmetry. The  $^2\text{H}$  NMR line shape of a dideuteron pair in the solid state as a function of tunnel and incoherent exchange rate is studied numerically. For single crystals, the effects of coherent and incoherent exchange are strongly different, in particular if the rate constants are on the order of the quadrupole splitting. The spectra of nonoriented powder samples are more similar to each other. Nevertheless, our calculations show that there are still pronounced differences, which should allow the distinction between coherent and incoherent exchange even in nonoriented samples.

### Introduction

The structure and dynamics of hydrogen in transition metal polyhydrides is a matter of current experimental and theoretical interest. Kubas et al.<sup>1,2</sup> found dihydrogen units  $\eta$ -bound to the transition metal. Today, a whole series of transition metal polyhydrides with hydrogen distances varying between 0.8 and 1.7 Å is available.<sup>3</sup> In these compounds the hydrogen atoms are mobile; in particular, they are subject to a mutual exchange, formally corresponding to  $180^\circ$  rotations involving a barrier with a height depending on the chemical structure. If the rotational barrier is zero, corresponding to free dihydrogen, the rotation is a coherent quantum process leading to even rotational states ( $p\text{-H}_2$ ) with antiparallel nuclear spins and to odd rotational states ( $o\text{-H}_2$ ) with parallel spins. When a rotational barrier is introduced by dihydrogen binding to a metal center, the energy splitting between the lowest  $p\text{-H}_2$  and  $o\text{-H}_2$  states corresponds to a coherent rotational tunnel splitting of frequency  $\nu_t$ . This splitting can be observed by inelastic neutron scattering<sup>2</sup> (INS) when the barrier is small and the splittings are on the order of terahertz. In the other extreme, when the barrier is large and the tunnel splitting becomes of the order of typical  $^1\text{H}$  chemical shift differences (i.e., hertz to kilohertz) the tunnel splitting gives rise to a quantum exchange coupling  $X_{12} = J_{\text{exch}}$  in the NMR spectra<sup>4,5</sup> of the hydride pairs, which can be observed if each hydride exhibits a different chemical shift.  $J_{\text{exch}}$  adds up with the usual scalar magnetic coupling  $J_{\text{magn}}$  to an effective  $J$

coupling, as was recognized by Zilm et al.<sup>5a–d</sup> and Weitekamp et al.<sup>5e</sup>  $J_{\text{exch}}$  represents an average over a large number of rovibrational states as it increases strongly with increasing temperature. On the other hand, superimposed on the coherent exchange are incoherent exchange processes, which also have been observed in the NMR spectra of these hydrides<sup>4,6,7</sup>. In the case of a HD pair, these incoherent processes correspond to H/D scrambling between the two different molecular sites in which the pair is located. In contrast to the quantum exchange, the incoherent exchange leads to a magnetic equivalence of the coupled hydrogen nuclei, i.e., to line broadening and coalescence. This process also leads to characteristic line shape changes in INS spectra<sup>2</sup> and affects the results of  $p\text{-H}_2$  induced nuclear spin polarization experiments.<sup>8</sup> These line shape changes can be described quantitatively in terms of the quantum-mechanical density matrix formalism developed by Alexander<sup>9</sup> and Binsch,<sup>10</sup> where only the nuclear spin degrees of freedom are treated quantummechanically and the spatial degrees of freedom (bath coordinates) are treated via phenomenological rate constants. The advantage of this formalism is that it is directly comparable to the NMR experiment, because NMR always measures the projection of the molecular system onto the spin system. Therefore it is possible to project the complex spatial dynamics of the problem onto these phenomenological rate constants that are measured in the NMR experiment. Thus a more detailed theory in the future only needs to reproduce these rate constants but not the NMR spectra from which these constants were extracted. We note that the phenomenological

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