^2H MAS NMR of strongly dipolar coupled deuterium pairs in transition metal dihydrides: extracting dipolar coupling and quadrupolar tensor orientations from the lineshape of spinning sidebands

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A selectively D_2 labeled transition metal dihydride, $\text{Os}(\text{D}_2)(\text{Cl})_2(\text{CO})(\text{P}^i\text{Pr}_3)_2$, was synthesized and studied by ^2H magic angle spinning (MAS) NMR spectroscopy. It was found that the interference between the quadrupolar and homonuclear dipolar interaction results in a characteristic lineshape of the MAS sidebands. The basic properties of the interference of homonuclear dipolar and quadrupolar coupling on the ^2H NMR lineshape were elucidated, using average Hamiltonian theory, and exact simulations of the experiments were achieved by stepwise integration of the equation of motion of the density matrix. These simulations show that it is possible to determine the size of the dipolar interaction and thus the D–D distance from the lineshape of the sidebands.

Introduction

Non-classical transition metal hydrides with η^2 -bonded dihydrogen ligands have very interesting physical, spectroscopic and chemical properties and are attracting much experimental and theoretical interest.^{1–23} Understanding their chemistry has led to a better understanding of catalysis since they may be catalyst precursors or stable models for short lived intermediate steps in catalysis.^{12,24–27} Following the pioneering work of Kubas *et al.*,^{28,29} a whole series of transition metal polyhydrides with hydrogen–hydrogen distances varying between 0.8 and 1.7 Å have been synthesized.^{20,30–34}

A property of dihydrogen complexes is that in many of these compounds the hydrogen atoms are not fixed in space as in conventional hydrogen bonds but can exchange their positions, either at higher temperature owing to conventional chemical exchange or at low temperatures owing to quantum mechanical tunneling, which has been shown in many studies.^{16,23,35–43} The quantitative interpretation of these dynamic processes depends strongly on the exact knowledge of the HH or DD distances; however it is no easy task to obtain accurate structural information about the hydrogen positions in these compounds in the solid state, for several reasons. There are the well known difficulties of X-ray diffraction in locating hydrogen positions. Single crystal neutron diffraction solves many of these difficulties but this elaborate technique is reserved for only a few important samples where large crystals are available. Even the dynamic behavior of the dihydrogen ligand in samples as cold as 10 K introduces uncertainties of up to 0.1 Å in the H–H distance.

In recent years, solid state NMR spectroscopy^{44–47} has evolved as an alternative approach towards distance and structure determination of solids, in particular when these systems exist in an amorphous or disordered phase. However,

most of the solid state NMR techniques available today are designed for the spectroscopy of either pairs of heteronuclei (*e.g.*, for pairs of spin-1/2 nuclei: separated local field (SLF),^{48,49} dipolar CSA spectroscopy^{50–52} and REDOR,^{53–55} or for a spin-1/2 coupled to a quadrupolar nucleus: CPL-REDOR,⁵⁶ TRAPDOR⁵⁷ and REAPDOR^{58,59}) or homonuclear pairs such as $^{13}\text{C}^{13}\text{C}$ ^{60–63} or $^1\text{H}^1\text{H}$.⁶⁴ Solid state ^1H NMR has been successfully applied to determine the H–H distance in a few samples where the distance is short.^{65–67} The presence of hydrogens on the other ligands of many dihydrogen complexes makes this technique difficult to apply.

However, if one is interested in distances between a homonuclear pair of quadrupolar nuclei (*e.g.*, in a dideuterium complex) the situation becomes difficult, since in this situation the strong quadrupolar interaction and the relatively weak homonuclear dipolar couplings, due to the usually low gyromagnetic ratios and the comparatively large distances, render it impossible to extract the distance information from the NMR spectra.

A possible exemption from these limitations is the η^2 -bonded dideuterium complexes, because first, many of them have short D–D distances with correspondingly strong dipolar couplings, and second, the quadrupolar couplings are relatively weak, typically in the range 50–100 kHz, due in part to the high mobility of the hydrons found in these compounds. In principle, it is possible to extract these homonuclear ^2H dipolar couplings directly from static ^2H NMR spectra by lineshape analysis. In practice, however, one will encounter two types of problems if static spectra are employed. First, there is a sensitivity problem in many of these systems due to the relatively low ^2H concentration in the sample. Second, since static ^2H quadrupolar spectra usually exhibit superimposed powder patterns from other ligand nuclei, very careful selective ^2H labeling of the sample is

necessary. This is often not feasible because unwanted chemical reactions take place in the sample that cause isotope fractionation. Such isotopic impurities make it impossible to distinguish the effects of the relatively weak dipolar couplings from sub-spectra of different isotopomers. For the solution of the sensitivity problem in the measurement of the DD distances in these compounds, a magic angle spinning (MAS) technique, which has higher sensitivity, is needed. As will be shown below, such a MAS technique aids also in the solution of the second problem, because the signals arising from the dipolar coupled deuterons are now clearly distinguishable from signals of other deuterons.

In a recent study of solid state ^2H NMR properties of some dideuterium complexes,⁶⁸ some of us observed features in the MAS spectrum of $\text{Os}(\text{D}_2)(\text{Cl})_2(\text{CO})(\text{P}^i\text{Pr}_3)_2$ attributed to a D–D dipolar–quadrupolar interference phenomenon. In the present work, we verified this finding and here we show that, indeed, by careful lineshape analysis of the MAS spinning sidebands, it is possible to elucidate the dipolar couplings and thus the DD distance from the MAS spectra.

This analysis is performed in two steps. First, the basic physical features of a system of two deuterons under the influence of sample spinning, dipolar interaction and quadrupolar interaction are elucidated from an average Hamiltonian analysis.⁶⁹ This analysis shows that the interplay of dipolar and quadrupolar coupling leads to a residual coupling between the two deuterons that is visible. However, as the quadrupolar coupling strength is about an order of magnitude stronger than the MAS rotation frequencies involved, it is evident that the Magnus expansion⁷⁰ will only slowly converge. Therefore, for a quantitative discussion of the model, numerical simulations are a necessary prerequisite that are performed as the second step.

These simulations can be performed in two different ways. In the first, a full numerical simulation of the ^2H NMR spectrum by stepwise integration of the kinetic equation of the density matrix is performed. Although this level provides the full quadrupolar sideband MAS spectrum, it has the strong disadvantage of a high computational cost required to treat accurately a spectral width that is large enough to avoid the folding-back of transitions and a frequency resolution that is fine enough to obtain a reasonable lineshape of the spinning sidebands. An alternative is therefore to calculate numerically the average propagator of the first rotation period and employ this propagator to calculate the spectrum of the average Hamiltonian. While this approach does not deliver any information about the sideband intensities, it is numerically about a factor of five faster and the resulting spectra are easier to compare with the experimental results.

Experimental

The sample of $\text{Os}(\text{D}_2)(\text{Cl})_2(\text{CO})(\text{P}^i\text{Pr}_3)_2$ (Fig. 1) was prepared as described elsewhere.⁶⁸ It is important to note that in this sample preparation some residual hydrogen is present as HD. The HD and DD fractions will both contribute to the ^2H

Fig. 1 Chemical structure of 1.

NMR spectra and cause an overlap in the lineshape. However, only the DD fraction will exhibit homonuclear dipolar coupling, which can result in an inhomogeneous line broadening, while the HD fraction will contribute only a narrow line under MAS conditions with high power ^1H decoupling. In particular, the ^1H solution NMR of the sample revealed a small amount of HD, which can be estimated to be below 20% of the amount of DD.

The compound was sealed in a standard 5 mm NMR tube 30 mm in length under 1 atm of N_2 . The spectra were collected on a Bruker ASX 200 NMR spectrometer operating at 30.72 MHz for ^2H . The ^2H CPMAS spectra were acquired by placing the sample tube in a Bruker 7 mm od zirconia stretch rotor. The Hartman–Hahn match was set directly on the sample and the spectra were collected with high power proton decoupling during the acquisition. The ^1H 90° pulse was 4.0 μs and the contact time was 3 ms. 16K time domain points were collected with a spectral width of 150 kHz using a 10 s relaxation delay. One spectrum was collected with a spinning speed of 4 kHz for 18.5 h and another with a spinning speed of 1885 Hz for 1.75 h.

Results and discussion

Analytical results

In the following, an analytical theory of a system of two chemically equivalent deuterons under the influence of their individual quadrupolar interactions, dipolar interactions and sample spinning is developed. Owing to the chemical equivalence of the two deuterons, one can assume a general C_{2v} symmetry of the problem, which results in the following assumptions for the general case: the M–D₂ plane is a mirror plane of the system and thus both quadrupolar tensors have the normal of the M–D₂ plane as a common principal axis. From this it follows directly that the relative orientation of the two tensors is describable by a single angle, namely the angle between the main principal axis and the C_2 axis. Note that this axis does not necessarily coincide with the M–D or DD bond axis. Moreover, the axis of the dipolar interaction is per-

Fig. 2 Coordinate system used for describing the relative spatial orientation of the two quadrupolar tensors of deuterons D₁ and D₂. C_{2v} symmetry is assumed for the deuterons and therefore one of the principal axis (q_{yy}) is parallel to y . The quadrupolar tensor of deuteron 2 is obtained by a 180° rotation around the z -axis of the coordinate system. For describing the relative orientations of the tensors it is more convenient to use the angle between the z -axis and the q_{zz} component. Note that in general the bond angle 2α will not coincide with the jump angle 2β , i.e., $2\alpha \neq \beta$.

pendicular to the C_2 axis. A coordinate system is chosen according to this symmetry (Fig. 2) in such a way that the z -axis bisects the D–M–D bond angle and that the y -axis is perpendicular to the D–M–D bond plane. The two quadrupolar tensors are related by a rotation $\mathbf{R}$ with angles $\pm\beta$ around the y -axis of the coordinate system. The angle β depends on the strength of the electric field gradients (EFG) caused by the metal and by the other deuterons. In particular in the case of a dihydride, β will be half the bond angle 2α (i.e., $\beta = \alpha$). For molecular dihydrogen with a very weak interaction with the metal or dihydrogen complexes where the M–D bonding is negligible compared with the D–D bonding, the two quadrupolar tensors will have their z -axis in the direction of the D–D axis, i.e., $\beta = \pi/2$. For simplicity we shall call these complexes “nascent” dihydrogen complexes. The dipolar interaction tensor, which is parallel to the DD vector, is thus perpendicular to the z -direction and points in the x -direction.

First the general theory of the sideband spectra is developed. Subsequently, the special case of collinear quadrupolar tensors, due to the effect of fast motional exchange or rotation, is examined. In this situation both tensors become equivalent and symmetry relations lead to a drastic simplification of the problem.

General case. A homonuclear spin pair of two chemically equivalent, dipolar coupled deuterons in a solid has a high field MAS NMR Hamiltonian of the form

$$H(t) = \omega_D(t)(2I_z S_z - I_x S_x - I_y S_y) + \omega_{QS}(t)(S_z^2 - \frac{2}{3}) + \omega_{QI}(t)(I_z^2 - \frac{2}{3}) \quad (1)$$

where the time dependent coefficients are due to the sample spinning; $\omega_{QS}(t)$ and $\omega_{QI}(t)$ are the quadrupolar interactions and $\omega_D(t)$ is the dipolar coupling between the I and S spins. Terms corresponding to off-resonance and chemical shift anisotropy (CSA) are one order of magnitude smaller than the homonuclear interaction at accessible field strengths and are therefore omitted.

The dipolar coupling coefficient $\omega_D(t)$ depends on the distance between the two spins and the time dependent angle $\nu(t)$ between the internuclear vector and the external magnetic field direction:

$$\begin{aligned} \omega_D(t) &= \frac{\mu_0}{4} \hbar \frac{\gamma^I \gamma^S}{r^3} \{3 \cos[\mathcal{G}(t)]^2 - 1\} \\ &= \frac{D}{2} \{3 \cos[\mathcal{G}(t)]^2 - 1\} \end{aligned} \quad (2)$$

Since both deuterons are chemically equivalent, the differences in their quadrupolar interaction are due to different orientations of their individual quadrupolar tensor with respect to the external magnetic field. For the forthcoming discussion it is advantageous to replace the individual quadrupolar interactions by the sum and the difference of the quadrupolar interactions:

$$\begin{aligned} Q &= \frac{1}{2}[\omega_{QS}(t) + \omega_{QI}(t)] \\ q &= \frac{1}{2}[\omega_{QS}(t) - \omega_{QI}(t)] \\ d &= \omega_D(t) \end{aligned} \quad (3)$$

Assuming numbering of the eigenstates as

$$\begin{aligned} |1\rangle &\equiv |++\rangle & |2\rangle &\equiv |+-\rangle & |3\rangle &\equiv |-+\rangle \\ |4\rangle &\equiv |0+\rangle & |5\rangle &\equiv |00\rangle & |6\rangle &\equiv |0-\rangle \\ |7\rangle &\equiv |--\rangle & |8\rangle &\equiv |-0\rangle & |9\rangle &\equiv |- -\rangle \end{aligned} \quad (4)$$

The Hamiltonian is block-diagonal and can be expressed as a direct sum of fictitious spin-1/2 and fictitious spin-1 operators ($S_k^{n,m}$ and $S_k^{n,m,o}$ denote the usual spin operators and $E^{n,m}$ and $E^{n,m,o}$ the identity matrix in these subspaces):

$$\begin{aligned} H &= \left[2\left(\frac{Q}{3} + d\right) E^{1,9} \right] \\ &\oplus \left(-\frac{Q}{3} E^{2,4} + 2q S_z^{2,4} - 2d S_x^{2,4} \right) \\ &\oplus \left(-\frac{Q}{3} E^{6,8} - 2q S_z^{6,8} - 2d S_x^{6,8} \right) \\ &\oplus \{ -\sqrt{2} d S_x^{3,5,7} + 2(Q-d)[(S_z^{3,5,7})^2 - \frac{2}{3}] - \frac{4}{3} d E^{3,5,7} \} \\ &= H^{1,9} \oplus H^{2,4} \oplus H^{6,8} \oplus H^{3,5,7} \end{aligned} \quad (5)$$

The different subspaces are orthogonal with respect to each other and thus operators of different subspaces commute and can be treated independently of each other.

A general analysis of the ^2H NMR spectra of this system would only be feasible by employing Floquet theory.^{71–73} However, as the rotation frequencies are much smaller than the quadrupolar interactions, a relatively large set of Floquet base states would be necessary to describe the spectra. Since we are mainly interested in understanding the appearance of the static, i.e., time independent, part in the signal, it is easier to calculate this static part by calculating the average propagator during one rotor cycle. For a quantitative analysis a numerical calculation of the average spectra is necessary (see below). For the study of the basic features of the system, however, it is more useful to analyze the system employing average Hamiltonian theory, which will be done in the following.

Using the well known Magnus expansion, the first two parts of the average Hamiltonian expansion are^{69,70}

$$\bar{H}^0 = \frac{1}{T_{\text{ROT}}} \int_0^{T_{\text{ROT}}} dt_1 H(t_1) \quad (6)$$

$$\bar{H}^1 = \frac{-i}{2T_{\text{ROT}}} \int_0^{T_{\text{ROT}}} dt_2 \int_0^{t_2} dt_1 [H(t_2), H(t_1)] \quad (7)$$

The time dependence of q , Q and d can be described as harmonic functions f_μ ($\mu = q, Q, d$), of the following type ($\Omega = 2\pi/T_{\text{ROT}}$):⁴⁷

$$\begin{aligned} f_\mu(t) &= C_{1\mu} \cos(\Omega t) + C_{2\mu} \cos(2\Omega t) \\ &\quad + S_{1\mu} \sin(\Omega t) + S_{2\mu} \sin(2\Omega t) \end{aligned} \quad (8)$$

where $C_{1\mu}$, $C_{2\mu}$, $S_{1\mu}$ and $S_{2\mu}$ are real orientation dependent constants which depend on the initial orientation of the tensor. They average to zero over one rotor period:

$$\bar{f}_\mu = \frac{1}{T_{\text{ROT}}} \int_0^{T_{\text{ROT}}} dt_1 f_\mu(t_1) = 0 \quad (9)$$

Therefore, the zero order average Hamiltonian disappears for all subspaces of eqn. (5):

$$\bar{H}^0 = 0 \quad (10)$$

In the first order average Hamiltonian, however, products of the following type appear:

$$\bar{f}_{\mu\nu} = \frac{1}{T_{\text{ROT}}} \int_0^{T_{\text{ROT}}} dt_2 \int_0^{t_2} dt_1 f_\mu(t_1) f_\nu(t_2) \quad (11)$$

which will in general be different from zero, owing to terms of the type $\cos^2(\Omega t)$, $\cos^2(2\Omega t)$, $\sin^2(\Omega t)$, $\sin^2(2\Omega t)$, and thus contribute to the static part of the interaction. The first order

average Hamiltonian resulting from eqns. (5) and (7) is

$$\begin{aligned}\bar{H}^1 &= \frac{1}{\Omega} (2s_{1d}c_{1q} - 2s_{1q}c_{1d} + s_{2d}c_{2q} - s_{2q}c_{2d})S_y^{2,4} \\ &\oplus \frac{-1}{\Omega} (2s_{1d}c_{1q} - 2s_{1q}c_{1d} + s_{2d}c_{2q} - s_{2q}c_{2d})S_y^{6,8} \\ &\oplus \frac{1}{\sqrt{2}\Omega} (2s_{1d}c_{1Q} - 2s_{1Q}c_{1d} + s_{2d}c_{2Q} - s_{2Q}c_{2d}) \\ &\quad \times (S_y^{3,5,7}S_z^{3,5,7} + S_z^{3,5,7}S_y^{3,5,7}) \\ &= \frac{\omega_\Delta}{\Omega} [S_y^{2,4} \oplus (-S_y^{6,8})] \oplus \frac{\omega_\Sigma}{\Omega} \\ &\quad \times (S_y^{3,5,7}S_z^{3,5,7} + S_z^{3,5,7}S_y^{3,5,7})\end{aligned}\quad (12)$$

where we have introduced the frequencies ω_Δ and ω_Σ as abbreviations for the terms in the brackets (Σ and Δ denote that they stem from the sum and difference of the quadrupolar frequencies, respectively). Note that even for collinear quadrupolar tensors ($q = 0$, see below), the first order average Hamiltonian does not disappear, owing to the term with ω_Σ .

Fast exchange. In the case of fast exchange of the two deuterons, their quadrupolar tensors and hence their quadrupolar frequencies become identical, *i.e.*, $q = 0$. In this situation, it follows from symmetry that the tensors have one principal axis parallel to the C_2 axis and the other parallel to the DD vector. Moreover, in this situation the quadrupolar tensor and the dipolar tensor have a common PAS (principle axes system).

The Hamiltonian is invariant under a permutation of the two deuterons and it follows from group theory that the Hamiltonian can be reduced into a block with **a** symmetry and a block with **b** symmetry, by using the eigenvectors of the permutation operator as a symmetry adapted base set. Ordering the symmetry adapted base functions as follows:

$$\begin{aligned}|a1\rangle &\equiv |00\rangle & |a2\rangle &\equiv \frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \\ |a3\rangle &\equiv |++\rangle & |a4\rangle &\equiv |--\rangle \\ |a5\rangle &\equiv \frac{|+0\rangle + |0+\rangle}{\sqrt{2}} & |a6\rangle &\equiv \frac{|0-\rangle + |-0\rangle}{\sqrt{2}} \\ |b1\rangle &\equiv \frac{|+0\rangle - |0+\rangle}{\sqrt{2}} & |b2\rangle &\equiv \frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \\ |b3\rangle &\equiv \frac{|0-\rangle - |-0\rangle}{\sqrt{2}}\end{aligned}\quad (13)$$

transforms the Hamiltonian into a block diagonal form that consists of one two-dimensional and seven one-dimensional subspaces:

$$\begin{aligned}\hat{H} &= \hat{H}_a \oplus \hat{H}_b \\ \hat{H}_a &= \begin{pmatrix} -\frac{4}{3}Q & -\sqrt{2}d \\ -\sqrt{2}d & \frac{2}{3}Q - 2d \end{pmatrix}^{1,2} \oplus (\frac{2}{3}Q + 2d)|a3\rangle\langle a3| \\ &\quad \oplus (\frac{2}{3}Q + 2d)|a4\rangle\langle a4| \\ &\quad \oplus (-\frac{1}{3}Q - 2d)|a5\rangle\langle a5| \oplus (-\frac{1}{3}Q - 2d)|a6\rangle\langle a6| \\ \hat{H}_b &= (-\frac{1}{3}Q + 2d)|b1\rangle\langle b1| \oplus (\frac{2}{3}Q - 2d)|b2\rangle\langle b2| \\ &\quad \oplus (-\frac{1}{3}Q + 2d)|b3\rangle\langle b3|\end{aligned}\quad (14)$$

This result has important consequences for the average propagator: it is evident that only the propagator in the 1,2 sub-

space is non-cyclic [*i.e.*, $U(\tau + nT_{\text{ROT}}) \neq U(\tau)$] and contributes to the average Hamiltonian. The average propagator in the 1,2 subspace is given as

$$U_{\text{AVR}}^{1,2} = T \exp \left[-i \int_0^{T_{\text{ROT}}} H_a^{1,2}(t) dt \right] \quad (15)$$

which can be employed to calculate the terms of the Magnus expansion, according to eqns. (6) and (7).

Numerical calculations

As already mentioned above, for a quantitative analysis of the sideband lineshapes, numerical calculations have to be performed. For the numerical calculation of the average Hamiltonian (H_{AVR}) spectra, first the average propagator of the first rotation period U_{AVR} was numerically calculated and diagonalized. In the next step the initial density matrix ($F_x = S_x + I_x$) and detection operator ($F_+ = S_+ + I_+$) were transformed into the eigenbase of U_{AVR} . These transformed operators were employed to calculate the free induction decay [$M_+(t) = \langle F_+ \rangle$] of H_{AVR} , which after numerical Fourier transformation gives the spectrum of H_{AVR} , *i.e.* (T denotes time ordering of the product):

$$U_{\text{AVR}} = T \prod_k \exp[-iH(t_k)\Delta t]$$

$$U_D = S U_{\text{AVR}} S^{-1}; F_{D+} = S F_+ S^{-1}; F_{Dx} = S F_x S^{-1}$$

$$M_+(nT_{\text{ROT}}) = \text{Tr}[F_{D+} U_D^n F_{Dx} U_D^{-n}] \quad (16)$$

For the calculation of the sideband spectra, this algorithm was expanded in the following way: the rotor period was subdivided into N equidistant time steps and for each step the average propagator over one cycle and the density matrix at this step of the first rotor period were calculated. Using these propagators and initial density matrices, the sub-FIDs were calculated in the same way as above and combined with the full FID, which after numerical Fourier transformation gives the spectrum. We found this algorithm to be about three times faster than the direct calculation with cyclic reuse of the propagator steps. Numerical powder integration was performed employing the optimized ZCW angle sets⁷⁴⁻⁷⁶ using the set of 3722 angles. All calculations were performed in the MATLAB 5.3 environment using laboratory-written MAS simulation software. The typical time for calculating a numerical sideband spectrum is about 1 h on a Pentium II at 233 MHz, compared with *ca.* 12 min for an AVH spectrum.

Experimental results

Fig. 3 displays the slow spinning (1885 Hz) ^2H MAS NMR spectrum of **1** at 30.7 MHz. As mentioned above, some

Fig. 3 Slow spinning (1885 Hz) ^2H MAS NMR spectrum of **1** and fitted sideband envelope ($Q_{zz} = 41\text{kHz}$ and $\eta = 0.8$). Note the broadening of the bases of the sidebands.

isotope fractionation occurs during sample preparation. Thus the ^2H MAS NMR spectrum is a superposition of the DD and the HD spectra with unknown concentration ratio. Assuming that the quadrupolar tensor is mainly determined by the local geometry of the deuteron and that HH/HD isotope effects can be neglected in first order, one can assume that both tensors will be similar and that both subspectra can be described by a common quadrupolar tensor (see also discussion of DD/HD content below). Owing to the slow spinning speed, the shape of the envelope of the individual sidebands is still close to the lineshape of the powder spectrum and can be employed as a measure of the reorientationally averaged quadrupolar tensor. Fitting the envelope results in $Q_{zz} = 41$ kHz, and $\eta = 0.8$, i.e., a highly asymmetric quadrupolar tensor.

A striking feature of the MAS spectrum is the broadening of the base of the individual sidebands, which is even more visible in the spectrum obtained at a 4000 Hz spinning speed (Fig. 4). The enlargement shows that the lineshape of the individual sidebands resembles a typical Pake lineshape with additional spectral intensity in the center of the sideband. On closer inspection of the lineshape of these sidebands, it is evident that there is some variation in the actual width and form of the lineshape as a function of the sideband order.

Numerical results

The question arises of what the origin of this structural feature of the lineshape is. To answer this question, we performed

Fig. 4 ^2H MAS NMR spectrum of 1 obtained at a 4000 Hz spinning speed and enlargement of the central two side bands (dashed box). Note that the sidebands clearly exhibit a Pake-like shape.

Fig. 5 Comparison of line-shape of ^2H NMR MAS sideband spectrum and MAS AVH spectrum ($\nu_{\text{ROT}} = 4000$ Hz, $D = 3.2$ kHz) at two different mutual orientations of the quadrupolar tensor ($2\beta = 0^\circ$ and 90°). Upper row, full sideband spectra; central row, enlargement of the central side band; lower row, AVH spectra.

numerical simulations of the full MAS line and of the average Hamiltonian (AVH), using the values of the quadrupolar interaction determined from the slow spinning spectra for characterizing the quadrupolar tensors. In a first step we were interested in the question of whether the AVH spectra can be employed as a good approximation of the sideband lineshape. The resulting simulations are shown in Fig. 5. The upper part displays the simulated MAS spectrum and an enlargement of the central line to see the structure of the sideband spectra. The lower part of Fig. 5 displays the sideband lineshape calculated from the numerical average Hamiltonian, with the same parameters as above. It is evident that the AVH spectrum gives a good approximation of the sideband lineshape obtained by the full simulation of the spectrum. Hence the much faster AVH calculations can be used to study the dependence of the sideband lineshape on the relative orientations and strength of quadrupolar and dipolar interaction tensors.

In the next step, the dependence of the AVH spectra on the strength of the dipolar interaction and mutual orientation of the two quadrupolar tensors was analyzed.

Fig. 6 displays the results of the calculation of the orientation dependence of the AVH spectrum for an ambient dipolar coupling of 2.5 kHz at 4 kHz rotation frequency. A clear change of the lineshape is visible, showing that it is possible to infer the mutual orientation of the two quadrupolar tensors from the MAS sideband spectra. For all orientations the outer parts of the spectra resemble a Pake⁷⁷ line. Moreover, the spectra close to $2\beta = 0^\circ$ exhibit an additional central component.

Fig. 7 displays the results of the calculation of the dependence of the AVH spectra on the strength of the dipolar couplings for two different orientations, namely $2\beta = 0^\circ$ and $2\beta = 90^\circ$. In both cases a broadening of the Pake-like part of the spectrum is observed. In addition, all spectra obtained at $2\beta = 0^\circ$ exhibit the central component. Comparing the width

Fig. 6 Numerical simulation of the orientation dependence of the average Hamiltonian spectra ($\nu_{\text{ROT}} = 4000$ Hz, $D = 2.5$ kHz). Left, contour plot; right, lineshapes.

Fig. 7 Numerical simulation of the average Hamiltonian spectra as a function of the strength of the dipolar coupling at $\nu_{\text{ROT}} = 4000$ Hz) for two different orientations of the quadrupolar tensors: left, $2\beta = 0^\circ$; right, $2\beta = 90^\circ$.

of the Pake-like component, it is evident that the spectra obtained at $2\beta = 90^\circ$ generally exhibit a larger linewidth.

One immediate consequence of these results is that the degree of ^2H isotope labeling achieved is of only minor importance for the interpretation of the lineshape of the sideband spectra. Signals of deuterons without homonuclear dipolar interaction will appear in the center of the spinning sideband and only strongly dipolar coupled deuterons contribute to the Pake-like components of the side band. Therefore, while it is still convenient to apply some isotope labeling to reduce the amount of signal from other deuterons, the degree of labeling is no longer a serious problem.

We then tried to fit the experimental spectrum to determine the dipolar coupling and thus the distance between the two deuterons and the mutual orientation of their quadrupolar tensors. As mentioned above, the shape of the experimental sidebands varies slightly as a function of the sideband order. Therefore, it would have been necessary either to simulate the full MAS spectra or alternatively to reduce the experimental spectrum to a pseudo-AVH spectrum. The latter approach is more attractive since the AVH calculation is about five times faster. Therefore, a collapsed sideband spectrum was calculated by averaging the inner 20 sidebands of the experimental spectra. This collapsed sideband spectrum was compared with the calculated AVH spectra. The best fit (Fig. 8) was obtained for $D = 3.2 \pm 0.2$ kHz, corresponding to 0.96 ± 0.02 Å and an angle of $2\beta = 0^\circ$ for the mutual orientation of the tensors. Fig. 9 finally displays the full simulated sideband spectrum employing the data from the AVH spectrum. Note the excellent agreement of the shape of the central sidebands with the

shape of the experimental sidebands shown in Fig. 4. Comparing the full spectra, there are some small deviations in the intensities of the outer sidebands, in particular in the region of ± 30 kHz, where some additional spectral intensity is visible in the experimental spectra. This additional intensity is an indication of the HD content of the sample, caused by the isotope fractionation discussed above.

The result of $2\beta = 0^\circ$ corroborates the assumed fast exchange of the two deuterons which leads to the symmetry considerations discussed above. Moreover the good coincidence between simulation and the experimental spectrum suggests that most of the intensity in the central sharp peak is associated with the D_2 signal; it was previously thought that this signal was due to an HD contaminant that formed by some H/D fractionation process during the synthesis. A small HD signal (estimated to be 20% HD–80% D_2) was observed in an NMR spectrum of the sample in solution. It is possible that the solid state contamination by HD is less than that estimated from this solution spectrum because the HD contaminant might have formed while the sample was dissolved.

It is interesting to compare the D–D distance obtained from the AVH spectrum with the distance obtained from the H–H isotopomer. In solution an H–H distance of between 0.9 and 1.1 Å was estimated from the minimum T_1 of the H_2 complex, with the 1.1 Å value considered to be more likely on the basis of the small $^1J(\text{HD})$ value of the HD isotopomer.^{78,79} Hence the D–D distance is comparable to the H–H distance but slightly shorter. Although part of this shortening could be the result of the DD stretching vibration, which, due to the $\langle r^{-3} \rangle$ averaging of NMR, favors shorter distances, it is also an indication of an isotope effect on the distance, possibly due to a shift of the average deuteron positions in the anharmonic potential.

Conclusion

It has been shown that homonuclear dipolar coupling among two chemically equivalent deuterons leads to a characteristic structure of the spinning sidebands, which depends on the strength of their dipolar coupling and the mutual orientation of their individual quadrupolar tensors. While the basic features of this coupling could be elucidated from analytical AVH calculations, a quantitative evaluation necessitates a numerical simulation either of the full MAS sideband spectrum or of the AVH spectrum. As an application of these calculations, the dipolar coupling between two deuterons in an η -bonded transition metal complex was analyzed. Indications of an H/D isotope effect on the D–D distance were found. Thus it is now possible to determine distances and mutual orientations in these compounds and to determine, for example, isotope effects on these distances, which are of great importance for the understanding of their catalytic properties.

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Fig. 8 Comparison of the collapsed experimental sideband spectrum and the fitted average Hamiltonian spectrum ($\nu_{\text{ROT}} = 4000$ Hz, $2\beta = 0^\circ$, $D = 3.2$ kHz).

Fig. 9 Numerical simulation of the experimental spectra shown in Fig. 4 and the inner two sidebands ($\nu_{\text{ROT}} = 4000$ Hz, $2\beta = 0^\circ$, $D = 3.2$ kHz) and enlargement of the central sidebands (dashed box).

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