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In this report, the application of a class of separated local field NMR experiments named dipolar chemical shift correlation (DIPSHIFT) for probing motions in the intermediate regime is discussed. Simple analytical procedures based on the Anderson–Weiss (AW) approximation are presented. In order to establish limits of validity of the AW based formulas, a comparison with spin dynamics simulations based on the solution of the stochastic Liouville–von-Neumann equation is presented. It is shown that at short evolution times (less than 30% of the rotor period), the AW based formulas are suitable for fitting the DIPSHIFT curves and extracting kinetic parameters even in the case of jump-like motions. However, full spin dynamics simulations provide a more reliable treatment and extend the frequency range of the molecular motions accessible by DIPSHIFT experiments. As an experimental test, molecular jumps of imidazol methyl sulfonate and trimethylsulfoxonium iodide, as well as the side-chain motions in the photoluminescent polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene], were characterized. Possible extensions are also discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2831798]

INTRODUCTION

Due to its strong dependence on the mutual distance between the interacting spins, the strength of the heteronuclear dipolar coupling is a valuable source for structural information. In order to resolve different chemical moieties in the NMR spectra, these distance measurements generally require magic-angle spinning (MAS). The magnitude of the dipolar coupling is, however, not only a valuable source to gain structural information but also for extracting dynamic parameters. The ratio between the experimentally determined reduced dipolar coupling and the rigid-lattice value, the order parameter, indicates fast molecular processes that average and, consequently, reduce the dipolar interaction.1 Besides the simple dipolar line-shape2 and relaxation experiments, some more elaborate approaches deserve special attention, namely, cross-polarization (CP) dynamics3 and separated local field (SLF) experiments. The first relies on the heteronuclear dipolar coupling between abundant (such as 1H) and rare spins (such as 13C) in CP experiments. The increase of the rare-spin magnetization occurs with the time constant \( T_{\text{CH}} \) that is—similar to the relaxation time \( T_1^{\text{CP}} \)—sensitive to dynamic processes in the kilohertz range and correlates to important mechanical parameters such as dynamic moduli. The measurement of \( T_{\text{CH}} \) became rather popular in dynamic investigations of organic solids.5 However, care must be taken in the interpretation of the data. A more straightforward experiment is the Lee–Goldburg (LG)-CP,7 in which the homonuclear 1H dipolar interaction is suppressed and the buildup curve of the rare-spin magnetization is governed by the 1H–13C interaction. SLF experiments provide a correlation between the chemical shifts and dipolar couplings. A popular version of SLF experiments is the wide-line separation, which was first suggested as a dynamic filter to separate mobile and rigid components in 13C spectra8 and was later turned into an easy-to-implement two-dimensional method.9 However, these experiments suffer from the simultaneous action of heteronuclear 13C–1H and homonuclear 1H–1H dipolar interactions, the latter masking the clear information provided by the former. An SLF variant that deserves particular attention is the efficient dipolar chemical shift correlation (DIPSHIFT) sequence.5,10,11 All these experiments determine the dipolar coupling strength that might be scaled down by fast molecular dynamics occurring with correlation times \( \tau_c \) within the range from \( 10^{-5} \) to \( 10^{-4} \) s. Information about the amplitude of the molecular process can be extracted from the order parameter reduction and most of the experiments mentioned above might be used for this purpose. The DIPSHIFT pulse sequence was identified to be a particularly robust experiment and is going to be used throughout this paper. Due to this reason, both the theory and simulations presented below are dedicated to this experiment.

The most important issue for studying molecular dynamic processes is to characterize both the motion amplitudes and time constants over a wide dynamic range, involving the application of several dynamic NMR methods. As discussed above, the usual applications of the SLF experiments are performed in the fast-motion regime, where they...
are only sensitive to the motion amplitudes. By slowing down the dynamic process by decreasing the temperature, one can reach the so-called intermediate-motion regime, at which the time constant of the dynamic process is similar to the inverse coupling constant of the anisotropic interaction. This scenario, which is mathematically very similar to the treatment of exchange NMR experiments, is well known in liquid-state NMR where the exchange of different isotropic frequencies leads to a loss of phase coherence and to a broadening of the spectra. The same approach is applicable for static solid-state spectra, where the exchange occurs between different anisotropic frequencies, i.e., between nuclei belonging to molecules with different orientations with respect to the external magnetic field. The approach is well developed and was applied frequently to H spectra in which the quadrupolar interaction is the dominating source of line broadening, making the calculation of the effect of molecular dynamic processes on the line shape relatively easy and straightforward. With MAS, however, a more elaborated theory is necessary to deal with the additional time dependence of the resonance frequencies, imposed by the MAS rotation. Qualitatively, the incoherent exchange processes interfere with the coherent time dependence of the MAS and spoil the periodicity of the time-domain signal, leading to a characteristic line broadening. Successful approaches to calculate spectra include the application of the Anderson–Weiss theory, Floquet theory, extended exchange theory, or stepwise numerical propagation in the framework of partial analytical solutions or of explicit density matrix simulations. In addition, in most of the cases for natural isotopic abundance nuclei in organic solids, dipolar decoupling has to be applied in concert with MAS to achieve appreciable spectral resolution. The H irradiation adds another coherent perturbation that interferes with the incoherent molecular exchange process and results in another source of line broadening. This effect was realized early and already put to use qualitatively. However, it is difficult to quantitatively simulate the spectra because it involves the relatively easy-to-handle chemical shift anisotropy (CSA) interaction as well as the more complicated hetero- and homonuclear dipolar interactions. Also, the actual line broadening spoils the spectral resolution, which is highly undesirable but partially unavoidable.

This prompts for a dynamic experiment that works in the intermediate-motion regime under the condition of natural abundance in organic solids, i.e., (i) it must permit the application of MAS and H decoupling during the acquisition period, (ii) should use a single and well-defined anisotropic interaction for probing the molecular dynamics, and (iii) for issues of spectral resolution, should be as little sensitive to dynamic line broadening as possible. In this paper we suggest the application of SLF experiments that correlate the 13C chemical shift resonances in a normal CP-MAS spectrum with the heteronuclear dipolar 1H-13C couplings. Since the 1H–1H coupling is efficiently suppressed by homonuclear decoupling sequences such as the LG or its advanced variants frequency switched Lee–Goldburg and phase modulated Lee–Goldburg, the 1H–13C interaction is predominant between a given 13C and the directly bonded 1H for aliphatic carbons. This interaction is axially symmetric and oriented along the C–H bond, which makes it a very convenient probe for the dynamic process. The poor spectral resolution is still an issue but can be partially worked around by the application of higher MAS rates that partially quench the line broadening effect. However, this also attenuates the heteronuclear dipolar coupling and makes the experiment less sensitive to the molecular dynamic processes. In turn, this can be partially overcome by the application of a DIPSHIFT variant that employs the recoupling of the 13C-1H dipolar interaction, i.e., measuring a multiple of the actual interaction strengths. Another disadvantage of the DIPSHIFT experiments is found when cross-polarization is used as the excitation scheme. The presence of internal motions during the contact time produces signal reduction. This problem becomes more severe when distribution of correlation times is present. In this case only part of the moving segments effectively contributes to the DIPSHIFT curves, decreasing the accuracy of the parameters measured under these circumstances. Alternatively, the intrinsic advantage of the SLF experiments is that only a specific interaction contributes to the signal and no extra experiment for data normalization is necessary.

In this report, we present the theory as well as experimental results for DIPSHIFT experiments applied in the intermediate-motion regime. For the extraction of kinetic parameters, the comparison of the experiments with calculated data is necessary. We present the numerical approach and discuss the influence of magnetic parameters of the sample as well as dynamic parameters on the calculated data. In addition, the accuracy and limits of validity of a fitting formula derived based on the Anderson–Weiss approach is discussed. The approach is applied to molecular jumps of imidazol methyl sulfoxide and trimethylsulfoxonium iodide (TMSI), as well as to the side-chain motion in the photoluminescent polymer poly[2-methoxy-5-(2’-ethoxyhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). Finally, we address possible extensions.

**METHOD AND MATERIALS**

The pulse sequence for the DIPSHIFT experiment is shown in Fig. 1(a). After the excitation procedure (CP, Direct polarization, etc.), the magnetization evolves during a variable time t under the influence of chemical shift and heteronuclear dipolar interaction, while the H homonuclear coupling is suppressed by H LG irradiation implemented in a phase modulated fashion (PMLG). The Hahn echo at t=0 removes the effect of chemical shift and leaves the H–13C dipolar coupling as the only effective interaction during the evolution time t. The signal detection under MAS during t is performed for different t values. The t-dependent modulation of the resulting line intensities in the spectra obtained can be used to extract the value of the H–13C dipolar coupling. In the case of fast dynamic processes, a reduced coupling is measured and can be turned into an order parameter of motion that in turn can be related to jump angles if a certain motional geometry is known or proposed, see Fig. 1(b). The models presented reflect the
TMSI is a test substance in which molecules undergo a well-evaluate the method. This sample was provided by Sluchter. Relevant kinetic parameters are known and can be used to characterize the motion. MEV-PPV is a semiconducting polymer in which the molecular dynamic processes directly affect its photoluminescent properties. In particular, it has been suggested that the MEH-PPV side chains perform three-site jumps with a distribution of correlation times. The MEH-PPV sample was obtained from Aldrich and used as received in the form of freestanding films cast from a concentrated chloroform solution.

**THEORY**

**Spin dynamics simulations**

The quantification of the DIPSHIFT data in the intermediate-motion regime can be performed using many approaches that describe the effects in this regime under MAS. This includes the Floquet theory,\textsuperscript{15,21} extended exchange theory,\textsuperscript{18–20} approximate theories based on the Anderson–Weiss theory,\textsuperscript{18–20} and stepwise numerical propagation\textsuperscript{24,25} using the solution of the stochastic Liouville–von-Neumann equation. Among these approaches, full spin dynamics simulations based on density matrix propagation were chosen to be employed here for the method validation. Specifically, a spin dynamics simulation program described by Saalwachter and Fischbach in Ref.\textsuperscript{25} was used. Since there is a comprehensive description of this approach in Ref.\textsuperscript{25}, the details of the simulation method are not going to be described here but only the main features that relate to the adaptation to our specific problem. Simply put, the simulation approach basically consists of a multistep calculation of the density matrix evolution under the effect of quantum-mechanical evolution under MAS and dynamic exchange. A specific feature of the program is that the quantum-mechanical (propagator-based) evolution of individual density matrices related to the different sites and mixing steps are performed independently in subsequent steps. This avoids the computationally costly diagonalization of the full Liouville-space propagator that embodies both quantum mechanics and exchange steps. In the particular case of the DIPSHIFT pulse sequence, three- and four-site jumps with a distribution of correlation times.

**FIG. 1.** (a) DIPSHIFT pulse sequence. (b) Depiction of some selected motional geometries, and (c) the behavior of the corresponding order parameters as a function of the motional amplitude (opening angle).

**FIG. 2.** Molecular structures of (a) imidazole methyl sulphonate, (b) trimethylsulfoxonium iodide (TMSI), and (c) [2-methoxy-5-[(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).
sequence, the evolution of CH (two spin system), CH$_2$ (three spin system), or CH$_3$ (four spin system) groups during $t_1$ was simulated considering off-resonance irradiation of the protons according to the LG conditions, i.e., the frequency offset was $\Delta \omega = \omega_0/\sqrt{2}$ so that the effective field is 54.7$^\circ$ away from the magnetic field direction. Thus, the scaling factor introduced by the use of the LG or PLMG irradiation is taken into account in the simulation. Because of the rotor-synchronized $\pi$ pulses, the chemical shifts are refocused in the pulse sequence and are not considered in the simulations. Another detail concerns the simulation of CH$_3$ groups, which was performed considering an average orientation of the protons among the three symmetric positions around the $C_3$ symmetry axis. This is equivalent to a fast rotation of the CH bonds around the $C_3$ axis.

To demonstrate the approach, we turn to the particular simple case of a two-site jump, as performed by the imidazole molecule, Fig. 2(a). Figure 3 shows theoretical DIPSHIFT dephasing curves, calculated with the parameters that describe the dynamics of the three symmetric positions around the $C_3$ symmetry axis. This is equivalent to a fast rotation of the CH bonds around the $C_3$ axis.

Analytical approaches based on the Anderson–Weiss approximation

The simulation procedure described above is very reliable and can be used to demonstrate the feasibility of using DIPSHIFT to study motions in the intermediate regime limit. However, there are some analytical treatments that are used to describe the evolution of nuclear spins under the simultaneous action of internal interactions (local fields), intermediate regime motions, and MAS. Because such approaches are easier to implement and can be used in a straightforward analysis, it is worthwhile to test the specific conditions under which they can be applied. Here we are going to discuss the analytical treatments based on the so-called Anderson–Weiss (AW) approximation, which has been successfully applied to describe the evolution of static and MAS spectra under the effect of diffusive motions. The first assumption of the AW approximation is that the distribution of local fields in the sample (due to the internal NMR interactions) corresponds to a stationary Gaussian frequency distribution. Further, fluctuations of these local fields are assumed to be fully random, and the stochastic loss of correlation is described by a monoeponential correlation function $g_{\text{therm}}(t) = \exp(-t/\tau_c)$, characterized by a single correlation time $\tau_c$. Note that spin diffusion in multiplet system, such as $^1$H nuclei in polycrystalline or amorphous samples, usually produces Gaussian frequency distributions (Van Vleck theory) and monoeponential correlation functions. This makes the AW approach particularly successful when employed for describing the dynamic evolution of $^1$H nuclei in organic powders, where the multiplet local fields lead to a “Gaussianization” and therefore to correlation loss by spin diffusion. Besides the stochastic loss of correlations assumed in the AW treatment, it is also necessary to introduce the coherent modulation due to the MAS. This was already done in several articles considering local fields produced by either chemical-shift anisotropy or dipolar couplings. A particularly successful approach was published first by Clough and Gray, further developed by Fenzke et al., and extended to consider diffusive anisotropic motion by Hirschinger. In
the latter case, i.e., diffusive anisotropic motions with order parameter $S^2 = \frac{(M_2)^{rigid}}{M_2} \left( \frac{1}{2} \right) f(\omega_R, 0, t) + \frac{t}{2} f(2\omega_R, 0, t)$

$+ (1 - S^2) \left[ \frac{t}{2} f(\omega_R, 1/\tau_C, t) + \frac{t}{2} f(\omega_R, 1/\tau_C, 1) \right]$, }

$f(\omega, 1/\tau_C, t) = \frac{\tau_C}{1 + (\omega \tau_C)^2} \left[ \frac{1}{2} \left( 1 - (\omega \tau_C)^2 \right) \right]$

$\times \left[ 1 - \exp \left( - \frac{t}{\tau_C} \right) \cos (\omega t) \right]$

$- \frac{2\omega^2 \tau_C^2}{1 + (\omega \tau_C)^2} \exp \left( - \frac{t}{\tau_C} \right) \sin (\omega t), \quad (1)$

where $\omega_R$ is the angular MAS frequency, $\tau_C$ is the motion correlation time, and $M_2 = \langle \omega_D^2 \rangle = \frac{9}{20} (2\pi D_{app})^2$ with $D_{app}$ being the apparent dipolar coupling constant, i.e., the dipolar coupling constant multiplied by the LG scaling factor of 0.577. The use of the above formula allows us to calculate the MAS signal under the effect of molecular motions. Thus, if one considers the local field as being produced by the scaled C–H dipolar interaction, the points in $S(t)$ covering the range from 0 to $T_{ROT}$ describes the DIPSHIFT curves. However, because both models are based on the AW approximations and were restricted to small-step diffusive processes, it is expected that they might fail if these conditions are not fulfilled. Note that the Gaussian frequency distribution might be approximately
RESULTS AND DISCUSSIONS
Comparison between analytical approaches and spin dynamics simulations

In this section, DIPSHIFT curves obtained by spin dynamics simulations and analytical approaches based on AW approximations are compared. Since the simulation of the molecular motions in the spin dynamics program is performed by assuming a finite number of jumps between non-magnetically equivalent molecular sites, the motion geometry of imidazole methyl sulfonate, two-site jumps on a cone of 64° aperture, will be considered, see Fig. 2. Figure 4(a) shows comparisons among the DIPSHIFT curves obtained by the spin dynamics simulation and Eq. (1) in the rigid and fast limits. In the rigid limit, a simulation using the standard MAS formulas is also appended. The curves obtained by spin dynamics simulations and MAS equations were obtained considering a CH coupling strength $D_{CH} = 22.7$ kHz (C–H distance of 1.1 Å) which leads to $D_{app} = (0.577)D_{CH} = 13.1$ kHz and $M^2 = 3 \times 10^9$ (rad/s)$^2$. The calculation using Eq. (1) was performed using a rigid limit second moment of $M^2_{rigid} = 2.9 \times 10^9$ (rad/s)$^2$, which was chosen to fit the lower value of the spin dynamics simulated DIPSHIFT curve in the rigid limit. The order parameter ($S=0.55$) was adjusted to produce the same curve as the spin dynamics simulation in the fast limit. At a spinning frequency of 4 kHz, a good agreement is observed between the rigid limit patterns obtained by the spin dynamics program and MAS equation, but a considerable deviation is observed for the pattern obtained from Eq. (1). In principle, one could think that it would be due to the value of $M^2_{rigid}$, but even if this parameter is set freely, the shape of the curves remains quite different. However, the discrepancy is much smaller in the patterns obtained at 8 kHz spinning frequency. This behavior can be understood by considering the rule of the Gaussian frequency distribution required in the AW approximation. This condition is actually not fulfilled in the case of isolated C–H pairs spinning at 4 kHz because the shape of the stationary frequency distribution (MAS spectrum) still shows a Pake-like pattern, and therefore does not have any similarity with a Gaussian pattern, as considered in the calculations with Eq. (1). When the spinning frequency is increased to 8 kHz, the reduction of the sidebands makes the Gaussian approximation more realistic, and as a result the DIPSHIFT curves coincide. In the fast limit, the molecular motion produces a randomization of the distribution of dipolar local fields, leading to coinciding DIPSHIFT patterns when the order parameter $S$ is chosen appropriately. Note also that the initial part of all curves coincide, which arises from the fact that at small evolution times, the AW approximation is valid even for non-

Gaussian frequency distributions (simply, the curve in this regime is sensitive only to the second and not the higher moments of the distribution). Thus, this result shows that the use of analytical approaches based on the AW approximation would be possible only for short evolution times for any spinning speed, but it also points to a possibly better overall agreement at higher spinning frequencies (above 7 kHz for C–H groups). Despite that, it is not possible to state that the DIPSHIFT curves obtained by spin dynamics simulations and Eq. (1) will actually agree for intermediate motions. Hence, to investigate the limit validity of Eq. (1) in the intermediate regime, a set of spin dynamics simulations for jumps among different numbers of sites was carried out and compared with the results obtained via Eq. (1).

Figure 4(b) shows a set of spin dynamics simulations of the DIPSHIFT curves considering 2-, 3-, 8-, and 16-site jumps on a cone of aperture of 64° (see model in Fig. 2). For 3-, 8-, and 16-site jumps, all curves lie on top of each other, except for the 2-site jump process. For 3-, 8-, and 16-site jumps, the only effect of increasing the number of sites without changing the motion geometry is a constant factor in the relation between the correlation time and the apparent motional rates $\tau_C = 1/(N_k)$, which was taken into account in Fig. 4(b). Note also that the deviation between the curves for two- and $n$-site jumps decreases for shorter $t_1$ values and slower rates, but even in the short $t_1$ part of the curve, a deviation is still apparent. This is actually an unexpected behavior because for two-site jumps, the average tensor in the fast limit is asymmetric, which is not the case of multisite jumps. Figure 4(c) shows a comparison between DIPSHIFT curves obtained by spin dynamics simulations and Eq. (1). Except for the rigid and fast limit cases already discussed, the agreement between the two approaches is poor, in particular, at $t_1 = T_{ROT}$. However, at short $t_1$ values [see right hand side of Fig. 4(c)], the agreement is actually fairly good. In fact, this can be understood by considering that at short evolution times, no Gaussian distribution of frequencies is needed for the AW approximation, which makes Eq. (2) or (3) good approximations even for finite-site jump motions. This is an important point concerning the usefulness of DIPSHIFT experiment in the intermediate regime because keeping the right limit a simple formula can be used to quantify the data, providing a good estimate of the motional correlation times. The case considered above might be a quite unfavorable case for testing agreement between the spin dynamics simulation and the AW based formula because the spin dynamics simulation considers a single C–H pair (Pake-like frequency distribution) executing jump process. Nevertheless, even for this very unfavorable case, acceptable agreement was found between both approaches when short $t_1$ times are considered. Note that upon increasing the number of spins (CH$_2$ or CH$_3$ groups), the approach should be even better because the stationary frequency distribution becomes more “Gaussian-like.” This was actually confirmed by further simulations. Therefore, Eq. (1) seems to be a good approximation for describing the short $t_1$ values behavior of the DIPSHIFT curves even for jump motions and can be used for a quick estimation of the correlation times. A drawback of using Eq. (1) is that the apparent $T_2$ decay is not well pre-
dicted by the formula, so this approach can only be used to predict the part of the DIPSHIFT curves where the C–H coupling averaging occurs. This reduces the dynamic window of application to motions occurring with correlation times in the range of ~20–0.1 μs. In contrast, if the spin dynamics simulation is used, the dynamic window is expanded to between 1 ms and 0.1 μs. Note that this dynamic window is rather complementary to exchange experiments (1 s to 1 ms) and $T_1$ relaxation measurements (>10 ns).

At this point, we would like to stress the conceptual similarity of the presently described experiments with what became known as “dynamic MAS experiments.” Similar to the well-known chemical exchange in liquids or the dynamic line shape in solids, the MAS spectra exhibit a broadening of the MAS side bands when the MAS rate becomes comparable to the jump rate of the dynamic process. As emphasized by Suwelack et al., the actual broadening depends on the geometry of the process and only a treatment that takes this into account can provide reliable kinetic parameters from full fitting, which is to some extent the conclusion obtained from the DIPSHIFT simulations discussed above (a more complete discussion about such comparison is provided in the supplementary material). However, in the DIPSHIFT experiment, there is a well-defined limit as to when an analytical description can be used, which is an important advantage. Another drawback of the experimentally much simpler line-shape experiments is the fact that the line shape is not only governed by the interference of the molecular dynamic process with the MAS rotation, but also by the heteronuclear dipolar decoupling that is much more difficult to include in an analytical description or in the Floquet treatments. Qualitatively, in addition to the broadening that appears when the jump rate is on the order of the MAS rate (typically some kilohertz), another broadening sets in at higher temperatures when the molecular jump rate becomes comparable to the frequency of the $^1$H decoupling, which is of the order of some tens of kilohertz. As it is shown below, this leads to the deviation of the calculated line shapes from the experimental data. Note, however, that in the spin dynamics simulations of the DIPSHIFT, the LG decoupling was taken into account explicitly and, as a result, this effect is part predicted of the analysis. Yet, the fact that spin dynamics simulations and Eq. (1) agree at short $t_1$ values also shows that the interference with the time scale of the LG decoupling (the actual rf) is not too important. The reason is of course that DIPSHIFT is a constant-time approach, where the LG period is increased at the expense of normal cw decoupling, which both operate at similar radio frequencies.

**Analysis of the behavior of DIPSHIFT curves for complex motions**

In the previous section, we have shown some general characteristics of the DIPSHIFT curves. For that we used simplified motional models, usually involving single rates and jumps between specific angles. However, in many cases molecular motions in organic solids are much more complex and cannot be readily described by these simplified models. Two important features of these complex motions are the presence of distributions of reorientation angles and correlation times, making it important to analyze the behavior of the DIPSHIFT curves in such cases.

The first topic to be addressed is the dependence of the DIPSHIFT patterns on the reorientation angle. For this we consider two-site jump processes occurring with different angles. Figure 5(a) shows the behavior of the DIPSHIFT curves as a function of the reorientation angles for three motional rates. In the slow-motion limit [Fig. 5(a) left], the main effect of increasing the reorientation angle is to decrease the intensity at $t_1=T_{\text{ROT}}$, i.e., to reduce the effective $T_2$ decay. In the intermediate regime [Fig. 5(a) middle], there is a simultaneous reduction of the effective coupling and effective $T_2$.
decay for increasing reorientation angles, and in the fast regime [Fig. 5(a) right], only the effective coupling is reduced.

The usual variation that is under external control is a change in the motional rate (i.e., by varying the sample temperature), and the increase in the motional rate can (or cannot) be accompanied by a change in the motional amplitude. The discrimination between these effects is generally difficult, and the use of a combination of methods is usually required. However, the behavior of DIPSHIFT curves in the intermediate regime is indeed sensitive to such a phenomenon. As just mentioned, in the intermediate-motion regime, the effect of increasing the reorientation angle on the DIPSHIFT curves is to simultaneously reduce the effective CH coupling and the intensity at \( t = T_{\text{ROT}} \). Since this trend is common for any motional rate in this regime, it is also visible when the rate and the reorientation angle increase simultaneously. If we compare Fig. 5 (middle) and Fig. 3, where no changes in the reorientation occur, we realize that the evolution of the DIPSHIFT patterns as a function of the rate should be quite distinguishable. Thus, by monitoring the changes in the shape of the DIPSHIFT patterns as a function of temperature, it might be possible to identify this trend and associate it with a simultaneous increase of the motional rates and amplitude. However, this would always be just a hint, as the complexity of the motion or a change in the motion geometry might bias such a simple analysis. For a complete elucidation of the process, more specific experiments that are able to probe separately the dynamic (correlation times) and the geometric part (reorientation angles), e.g., exchange NMR experiments, should be used.

Another feature that can be addressed is the presence of reorientation angle distributions. Figure 5(b) shows a set of DIPSHIFT patterns for different motional rates considering a Gaussian distribution of reorientation angles centered at 0° with various widths. The same general behavior as in the case of just increasing single angle is observed but with a smaller scale of variation. Note that the wider the distribution is, the smaller the intensity is at \( I(t_1 = T_{\text{ROT}}) \), and the smaller the apparent coupling is at \( I(t_1 = T_{\text{ROT}}/2) \). This is best observed in a plot of the intensity ratio \( I(t_1 = T_{\text{ROT}})/I(t_1 = T_{\text{ROT}}/2) \) shown at the right side of Fig. 5(b).

Another usual feature found for complex motions is the presence of a distribution of correlation times/rates. Figure 6 shows simulated DIPSHIFT patterns for different widths of correlation time distributions, where three-site jumps on a cone with 54° opening angle are considered. Note that in the absence of a correlation time distribution [Fig. 6(a)], the intensity at \( t_1 = T_{\text{ROT}} \) varies basically between 0 and 1, while for the case of a log-Gaussian distribution with a width of two decades [Fig. 6(b)], this variation range is considerably smaller. It is actually rather straightforward to qualitatively realize the occurrence of a distribution. If the temperature-dependent data exhibit a smiley-like appearance, then a distribution is very likely. This was also the case for a reorientation angle distribution, but note that in Fig. 6(b), a decrease in the effective coupling with a simultaneous increase of the effective \( T_2 \) decay is observed. The quantitative treatment requires, of course, numerical calculations and comparisons with the experimental data. As another demonstration, Fig. 6(b) shows the curve for \( k = 10^5 \) Hz, i.e., for the case of maximum dynamic broadening or minimum apparent \( T_2 \), but with different distribution widths. It is obvious that the narrower the distribution is, the shorter the \( T_2 \) decay is at \( I(t_1 = T_{\text{ROT}}) \) and the smaller the apparent coupling is at \( I(t_1 = T_{\text{ROT}}/2) \). This is again shown clearer by the ratio \( I(t_1 = T_{\text{ROT}})/I(t_1 = T_{\text{ROT}}/2) \), which is on the order of 1 for no or a very narrow distribution but increases with increasing distribution width. Note again that this behavior is contrary to the one observed for a distribution of reorientation angles. Again, this can only serve as qualitative indicator, and a detailed analysis by numerical simulations is inevitable for quantitative results.

OTHER REMARKS

Despite the fact that the above approach seems to be feasible, there are two drawbacks that must be addressed. First, if cross polarization is used as the excitation method, the presence of a distribution of correlation times leads to a bias in the fitted distribution because of the signal decay during contact time. This holds, in particular, for segments deep in the intermediate regime (with rates \( \sim 10^3 \) Hz) (see the supplementary material). To minimize the signal decay, it is vital to keep the contact time in the CP as short as possible. Another possible procedure for minimizing the CP signal decay is to perform a CP and contact time optimization for each experimental temperature. The second point concerns the remote \( ^1H \) nuclei. The dipolar couplings between the nuclear spin of a given carbon and the remote \( ^1H \) nuclear spin is indeed significantly smaller than for directly bonded spins. However, these remote spins are very abundant in organic systems, which may lead to significant effects. In this sense, the two spin approach, as used here, might not be sufficient for a good description. Two cases can be discussed when considering remote spins. If they are rigid, their presence will only add a constant contribution to the DIPSHIFT curves. In this case they can actually help with the cross polarization, avoiding loss of signal due to
intermediate regime motions during the CP, as discussed above. In contrast, if they present some mobility, they might have some contribution to the shape of the DIPSHIFT curves. However, it is expected that the effect of the remote spin will only appear for long evolution times, which also points to the use of higher spinning frequencies in the DIPSHIFT experiments in order to reduce the maximum evolution times. Note that in experiments that uses recoupling, rotational echo double resonance (REDOR)-like experiments, the effect of remote spins is expected to be much higher because the evolution times are longer and the interaction is “amplified.” In the case of the DIPSHIFT experiments, at least according to our simulations, the effect of remote spins is not so important and two spin simulations should be adequate. In fact, the multispin scenario favors the application of the AW approximation, so the presence of remote spins also does.

**EXPERIMENTAL RESULTS**

Figure 7 compares experimental data versus temperature from imidazole methyl sulfonate together with spin dynamics simulations. The agreement is quite remarkable. By plotting the jump rates in an Arrhenius plot, we can extract an activation energy of 70 $\pm$ 5 kJ/mol, which again is in good agreement with previously obtained data.\(^3\) However, the melting of this compound prevents obtaining of the second part of the dephasing curves as shown in Fig. 7, i.e., the decrease of the apparent dipolar coupling. To cover the full dynamic range of the method, we turned to TMSI. Here, the three methyl groups are arranged in a tetrahedral symmetry and perform threefold jumps. The fast methyl rotation leads to a preaveraging of both the CSA as well as the dipolar tensor. Figure 8 shows temperature-dependent MAS spectra together with corresponding simulations. Note the discrepancies at higher temperatures, which are due to the interference of the molecular motion in the kilohertz range with the coherent $^1$H irradiation, which is another source of dynamic line broadening from the deterioration of the $^1$H-decoupling efficiency. This effect is not included in the line-shape simulation, and this is, as mentioned above, one of the crucial drawbacks of the dynamic MAS approach.

Figure 9 (top) shows experimental and simulated temperature-dependent dephasing curves. In Fig. 9 (bottom), the correlations times $\tau_c=(3k)^{-1}$ are plotted in an Arrhenius diagram, from which an activation energy of about 76 kJ/mol is extracted. As comparison, previous $^2$H line-shape data (see Fig. 5 from Ref. 12) are plotted, too. It can be seen that the two experimental methods yield similar data and that the DIPSHIFT is also sensitive to longer correlation times. This is expected as it is more sensitive for motions with rates of the order of the dipolar coupling (a few kilo-
hertz in this case), while for the $^2$H line shape, the width of the $^2$H spectrum (about 40 kHz) is the determining factor. Note that while the DIPSHIFT works in natural abundance, the $^2$H experiments require isotopic enrichment which is not feasible in all cases. Another comparison that is displayed in the Arrhenius plot is the correlation times obtained by the fitting of the short $t_1$ range of the experimental data ($t_1/T_{\text{ROT}}<0.3$) by Eq. (1) (AW approach). The agreement is indeed fairly good, showing that this approach can also be used. However, it should be mentioned that there is considerable error in the correlation times extracted from this approach in Fig. 9, which is mostly due to the poor sampling of our data for $t_1/T_{\text{ROT}}<0.3$. Actually, one important experimental detail of the DIPSHIFT experiment is that the sampling of the $t_1$ points should coincide with the LG period ($2\pi$ proton pulse during LG irradiation), which reduces the number of $t_1$ points.

Finally, we turn to the photoluminescent polymer MEH-PPV, which was already the subject of NMR investigations. It was shown that the $\beta$ relaxation, which is related to the optical and electric properties of the material is, due to the side-chain motion. Around room temperature, this motion is in the fast limit and, therefore, the CH carbon labeled as 11 in Fig. 2 is an ideal candidate for acquiring detailed dynamic information on this motion. The NMR spectrum of MEH-PPV as a function of temperature in Fig. 10(a) shows $^{13}$C CP/MAS temperature-dependent spectra of MEH-PPV. The line assignment (according to the chemical structure shown in Fig. 2) is given in the spectrum acquired at 353 K. It is obvious for carbon 11 that there is a temperature-dependent broadening of the resonances belonging to the side-chain carbons, while those of the main chain remain fairly constant, confirming a side-chain specific process that reaches the intermediate regime at lower temperatures. The broadenings can in principle be simulated using the procedures mentioned above. However, the very dense spectrum and the small degree of broadening would make this very ambiguous. Also, the knowledge about the principal CSA values as well as the orientations of the CSA tensors in the molecules would be necessary. A much more elegant approach is the DIPSHIFT that requires fitting of the dephasing curves for the different resonances, for which only the experimental line intensities are required. The use of the C–H dipolar coupling, for which the principal values and orientations are well known, makes it also much easier to interpret, as compared to the CSA interaction that needs to be simulated in the cases of dynamic MAS experiments. Also, from our experience with dynamic MAS experiments, we are confident that it would be impossible to perform an unambiguous simulation like the one presented below. In particular, the distribution of $\tau_C$ would be difficult to determine without prior knowledge. Of course, also for DIPSHIFT simulations an a priori knowledge of the motion geometry is desired. In the case of MEH-PPV, previous measurements have shown (using DIPSHIFT experiments) that the CH$_2$ group attached to the main chain (labeled 10 in Fig. 3) is rather rigid (no temperature dependence was detected in the DIPSHIFT curves of this group from −50 to 50 °C), while the CH group 11 is already mobile in this temperature range. This is
largely consistent with a motional model were the CH group 1
11 executes n-site jumps around the H2C10-11 CH bond, which suggests a model of n-site jumps on a cone with an opening defined by the relative orientation of the CH bond with respect to the C–C bond (ideally 109°). Note that the number of jump sites is undetermined, but as shown in Fig.
4, for symmetric jumps over more than two sites, all the DIPSHIFT curves lie on top of each other. Thus, for the sake of simulation time, we just consider three-site jumps. The possibility of a two-site jump was actually excluded by the value of the order parameter extracted from the DIPSHIFT curve at high temperature (fast limit).

Figure 10(b) exhibits the experimental and simulated data obtained for the CH carbon 11. Figure 10(b) (left) shows the experimental MEH-PPV DIPSHIFT curve obtained at −20 °C and a set of simulated curves for an average rate of ⟨K⟩=10³ Hz and Gaussian rates distributions with 0.0, 0.5, 1.0, 2.5, 2.0, 3.0, and 4.0 decades. As it can be observed, it is not possible to simulate the experimental data using a single correlation rate. It rather prompts for the assumption of a correlation time distribution of 2.0 decades, as it is frequently found in polymers.37,41 As discussed before, the behavior of the DIPSHIFT curves as a function of temperature also point to that. Figure 10(b) (right) shows experimental DIPSHIFT curves as a function of temperature. These curves could be well fitted by threefold jump with fixed geometry but with a log-Gaussian rate distribution of about two decades, centered at different ⟨K⟩ values. No corrections to account for the loss of CP signal due to intermediate motions were applied. This is justified by the presence of many rigid protons in the vicinity of the CH group 11, which reduces the bias CP effect substantially. Further experiments on this material, in particular, with the extension to slower motions and the application of exchange NMR methods, are in progress and will be presented elsewhere.

As a final point, we would like to place a comment on possible extensions and alternatives. The approach as described above might be improved in two directions. First, there is always the value of the intrinsic T2 decay that arises from imperfections of the LG-building block. This needs to be determined separately on a rigid sample. Second, when dealing with methyl groups, there is already a preaveraging of the dipolar coupling which reduces the variation range of the normalized intensities. The former would ask for a constant-time version of the experiment, while the latter can be solved by a version that enhances the effect of existing dipolar coupling in the experiment. Both requirements are fulfilled by the DIPSHIFT version introduced by Hong et al.11 The theory presented here is applicable for this method too; however, the simulation program of course has to be matched to the actual pulse sequence. Note that there is also an AW theory for recoupling of dipolar interactions that are described in Ref. 20 and can, in principle, be used, but the limits should be checked as done here.

CONCLUSIONS

We extended the application of the DIPSHIFT-NMR method, an SLF method that was designed to be applied in the fast-motion limit only, toward the quantification of intermediate-range motions. For that, a more elaborated numerical calculation approach is necessary; however, for special cases, the correlation time of motion can also be extracted from a simple formula based on the Anderson–Weiss approach and, thus, a truly model-free approach to obtain the kinetic parameters is provided. In conjunction with that, we have also discussed the signal loss due to the presence of intermediate regime motions during the cross-polarization transfer, and some strategies to avoid this loss are proposed. Although the NMR experiment itself is well known, its combination with the presented numerical routine opens up a new range of applications, overcoming some of the problems of line-shape experiments that had to be used so far. In fact, this approach closes the gap between solid-state exchange NMR experiments, which are sensitive to slow motions, and the original DIPSHIFT (or more general SLF) experiments for the fast processes.

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35 J. Vanvleck, Phys. Rev. 74, 1168 (1948).
39 See EPAPS Document No. E-JCPSA6-128-026805 for more details on dynamic MAS experiments and effect of intermediate regime motions in the cross-polarization CP under MAS. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).