

Communication

CONTRA: Improving the performance of dynamic investigations in natural abundance organic solids by mirror-symmetric constant-time CODEX

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Received 10 August 2007; revised 30 October 2007

Available online 6 November 2007

Abstract

We present a minor but essential modification to the CODEX 1D-MAS exchange experiment. The new CONTRA method, which requires minor changes of the original sequence only, has advantages over the previously introduced S-CODEX, since it is less sensitive to artefacts caused by finite pulse lengths. The performance of this variant, including the finite pulse effect, was confirmed by SIMPSON calculations and demonstrated on a number of dynamic systems.

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Keywords: Dynamic solid-state NMR; 1D-MAS exchange; CODEX; SIMPSON; CONTRA

1. Introduction

The macroscopic properties of organic solids depend not only on the molecular structure but also on the geometry and time scale of the molecular dynamics. To understand the relation between the nano and macro levels, it is important to be able to determine experimentally both the time scale as well as the geometry of molecular dynamic processes. Solid-state NMR is among the few methods which are capable of doing this. The time scale at which the molecular processes occur, spans many order of magnitude and NMR provides tools that cover this entire range and which provide partial overlap between ranges as well. However, particular interest is often focused on the so-called slow processes with correlation times on the order

of milliseconds to seconds. Solid-state exchange experiments, which are basically 2D experiments that correlate the orientation dependent resonance frequencies before and after an adjustable mixing period, cover this correlation time range and provide detailed dynamic information [1–3]. For the investigation of samples with low natural abundance such as ¹³C, it is further necessary to use MAS to provide sufficient spectral resolution and sensitivity, as well as to run these experiments in time-saving 1D-modes. Over the last decades, a number of experiments have been suggested for this approach [4–10], the most widely used one being the CODEX pulse sequence [8,9]. This basically includes two evolution periods, t_{evol} and t_{reconv} , separated by the mixing period t_{m} . During t_{evol} , the X-nucleus magnetization precesses under the effect of the chemical shift anisotropy (CSA) and the acquired dephasing at the end of t_{evol} depends on the orientation dependent resonance frequency of the nucleus. The magnetization is then stored along the z direction during a

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variable mixing period t_m and rephases during t_{reconv} . If no reorientational motion has happened during t_m , the dephasing is exactly canceled by the rephasing and a signal with full intensity is acquired. However, if the nucleus under consideration has changed its orientation during t_m , the resonance frequencies and thus the acquired phases during the two evolution periods are different and an attenuated signal is acquired. Running this experiment with different values of t_m permits the extraction of the correlation time of motion, τ_c . The de- and rephasing during t_{evol} and t_{reconv} is facilitated by the application of rotor-synchronous π pulses that—in a manner similar to REDOR [11,12]—enhance the dephasing efficiency. In fact, the dephasing scales with the product of the number of π -pulse cycles and the MAS period T_R , $N \cdot T_R$. It thus allows this experiment to be run even under fast MAS, where the decreased dephasing can be compensated by a larger number of π -pulse cycles, keeping the overall length of CSA recoupling cycles $t_{\text{evol}} + t_{\text{reconv}} = 2 \cdot t_{\text{evol}}$ constant.

To extract information about the geometry of motion, the CODEX sequence has to be applied with a constant length of the mixing period t_m , but with an increasing length of t_{evol} . The resulting CSA-dephasing curve contains information about the different orientations of the nucleus under consideration before and after t_m , i.e., about the geometry of the molecular dynamics. This can be qualitatively understood in the following way. While for small-angle motions a small difference between the resonance frequencies before and after t_m is expected, requiring many evolution cycles to achieve appreciable dephasing, for a large-angle motions larger differences in the resonance frequencies lead to rapid dephasing, reaching an asymptotic level quickly. In particular for large-angle motions, it is necessary to acquire data for short $2 \cdot t_{\text{evol}} = N \cdot T_R$, which means relatively fast spinning. In contrast, small-angle motions can be detected only at large values of t_{evol} which can be achieved conveniently by slow spinning, to avoid intolerable loss of intensity due to a large number N and thus, many π pulses. In order to avoid the need to combine data that were acquired at different spinning rates, we recently suggested the S-CODEX sequence [10] which controls the efficiency of CSA dephasing not by the length of t_{evol} but by displacing the odd-numbered π -pulses: if these are placed at $t_1 = T_R/2$, maximum dephasing is achieved (as in CODEX). Hypothetically, if they are applied at $t_1 = 0$, there is no dephasing at all. Running experiments as a function of t_1 between 0 and $T_R/2$ permits acquisition of an analogous CSA-recoupling curve as in the original CODEX, but with the benefits of having a constant time and constant MAS-rate experiment. In practice, however, artifacts are in particular associated with the finite pulse length of the π pulses. For example, at a MAS rate of 5 kHz it would be necessary to acquire ten data sets with t_1 values between 0 and $T_R/2$, and the delay between the leading even-numbered π -pulse and the 1st dephasing π pulses would be just 10 μ s. Assuming realistic π -pulse lengths of about 6–8 μ s, it is expected that there might be a substan-

tial undesired interference of the pulses with the dephasing, spoiling the evolution of the magnetization under the anisotropic interaction, in this case the CSA. Other effects might be errors in pulse-length and phase that arise from the inhomogeneous B_1 field across the sample and/or misadjustments. It would be desirable to minimize these effects as much as possible.

In this contribution, we present another alternative version of the constant-time CODEX experiment which we will name CONTRA (*Constant-Time Recoupling of Anisotropies*) throughout the paper. The crucial point is that—similar to the mirror-symmetric REDOR sequences [11,13]—dephasing π - pulses of two adjacent de- and rephasing periods are moved symmetrically around T_R , i.e., from $t_1 = 0$ forward towards $T_R/2$ and from $t_1 = 2T_R$ backward towards $3T_R/2$, respectively, rather than starting at $t_1 = 0$ and moving forward for all cycles, as suggested in the original S-CODEX version. As a consequence of the CONTRA sequence the number of recoupling cycles must always be an multiple of two. The latter necessity might lead to a loss of intensity for samples with short ^{13}C - T_2^* , however, the benefits as discussed in the forthcoming sections more than offset this minor drawback. We will discuss the advantages of this approach and discuss the effect of finite pulses, based on SIMPSON calculations. The new experiment will be demonstrated on the model substance DMS as well as on samples with more complex dynamic geometries, namely the amorphous polymer PMMA and a sugar glass.

2. Experimental

The pulse sequence of the original CODEX experiment is shown in Fig. 1a. The second mixing period t_z is basically a z -filter for the selection of magnetization components and acquisition of a reference experiment (for details, see [9]). In Fig. 1b, the originally improved version of the S-CODEX experiment is shown [10], where the dephasing π pulses all move forward (as in the mirror-asymmetric REDOR sequence [11]), while Fig. 1c displays the CONTRA modification suggested here (similar to the mirror-symmetric REDOR [11]). The modification seems to be minor; however, we will see in the theoretical section that it has an important consequence. Notice that while for S-CODEX any number of recoupling cycles is possible for implementing the sequence, for CONTRA it is always necessary an integer multiple of two. All π -pulse were cycled according to the XY8 scheme [14].

Experiments were performed on a VARIAN INOVA 400, utilizing a 7-mm VARIAN VT-CPMAS probe (Jacobson design). Typical rf parameters of $\pi/2$ pulse lengths, were 5 μ s for ^{13}C and 4 μ s for ^1H , constant-amplitude cross polarization time of 1 ms and about 60 kHz of ^1H Decoupling. The data acquisition was performed as described in [15], i.e., the data shown below is the ratio taken from the so-called exchange (S) and the reference experiment (S_0), S/S_0 .

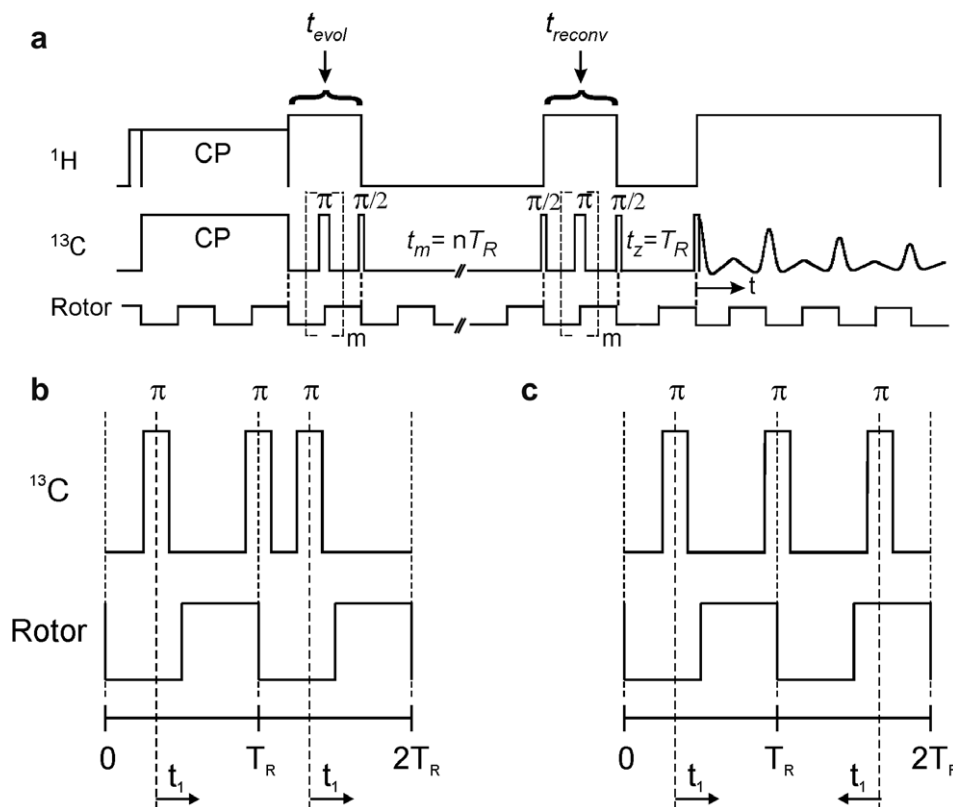


Fig. 1. (a) Pulse sequences of the CODEX experiment. Pulse-moving scheme of the CSA recoupling periods t_{evol} and t_{reconv} for (b) S-CODEX and (c) CONTRA. The length of the mixing period t_m must be actively synchronized with the MAS rotation.

DMS was purchased from SIGMA and used without further treatment. The PMMA sample was kindly provided by Dr. Mario Beiner, University of Halle, Institute of Physics. The Sugar glass is the amorphous sample of methyl α -L-rhamnopyranoside, Me-Rha, as described in [16].

3. Theory

We consider in the following the CSA interaction of an X-nucleus under MAS. The phase that a magnetization vectors acquires during free precession after a time t is given by

$$\begin{aligned} \phi^k(t) = \int_0^t \omega(t') dt' = & \frac{C_1^k}{\omega_R} \sin(\omega_R t' + \gamma) - \frac{S_1^k}{\omega_R} \cos(\omega_R t' + \gamma) \\ & + \frac{C_2^k}{2\omega_R} \sin(2\omega_R t' + 2\gamma) - \frac{S_2^k}{2\omega_R} \cos(2\omega_R t' + 2\gamma) \Big|_0^t \end{aligned} \quad (1)$$

where α , β , γ are the Euler angles relating the molecular frame of the molecule to the frame of the MAS rotor, and the terms $C_1^k(\alpha, \beta, \sigma_{nm}^k)$, $S_1^k(\dots)$, \dots depend on these angles as well as on the components of the CSA tensor, expressed in the molecular frame. Expressions for these coefficients can be found in [17,18]. The final CODEX signal for a molecule that resided initially at site i before and at site j after t_m is given by

$$S^{ij}(t_m) = \langle \cos(\Phi^i - \Phi^j) \rangle_{\alpha, \beta, \gamma} P_{ij}(t_m) \quad (2)$$

with $P_{ij}(t_m)$ being the probability to find a molecule at site j after t_m if it had been at site i before, $\langle \dots \rangle_{\alpha, \beta, \gamma}$ is the power average, and Φ^k is the phase acquired during the evolution periods at site j . For the cases discussed below, we assume that the experiments are all run in the limit $\tau_c \ll t_m$ and thus, $P_{ij}(t_m)$ becomes $1/N^2$ for equally populated sites, N being the number of accessible sites. The calculation of the so-called $N \cdot T_R$ -dependence thus reduces to the calculation of the term $\cos(\Phi^i - \Phi^j)$, which is affected by the timing of the π pulses (Fig. 1b and c). We will now briefly sketch this for the different CODEX variants.

Suppose we have a π -pulse train as displayed in Fig. 1b or c and number the times at which we apply the π pulses are t_1, t_2, \dots , keeping in mind that each π pulses inverts the phase of the magnetization that is evolving in the xy -plane, and that the even-numbered π pulses are always applied at integer multiples of T_R . The phase acquired after $2T_R$, i.e., after three π pulses, is given by

$$\Phi^k = \int_0^{t_1} \omega(t') dt' - \int_{t_1}^{T_R} \omega(t') dt' + \int_{T_R}^{t_3} \omega(t') dt' - \int_{t_3}^{2T_R} \omega(t') dt' \quad (3)$$

and, using the relation

$$\begin{aligned} \int_0^{T_R} \omega(t') dt' = 0 &= \int_0^t \omega(t') dt' + \int_t^{T_R} \omega(t') dt' \\ \rightarrow \int_0^{t_1} \omega(t') dt' &= - \int_{t_1}^{T_R} \omega(t') dt' \end{aligned} \quad (4)$$

it can be transformed into

$$\Phi^k = 2 \left(\int_0^t \omega(t') dt' + \int_{T_R}^{t^*} \omega(t') dt' \right) \quad (5)$$

where t and t^* are the times at which the first and third pulses are applied, respectively. These parameters are given for the three different CODEX versions in Table 1.

The calculation can be easily done using Eqs. (5) and (1). One ends up with 16 terms for Φ^k that reduce for the conventional CODEX (for two π -pulse cycles before and after t_m) to

$$8(\sin(\gamma) - \cos(\gamma)) \quad (6)$$

For clarity, we omit here the prefactors C_1^k/ω_R and S_1^k/ω_R from Eq. (1), and will continue to do so below. For both S-CODEX and CONTRA sequences, $\omega_R t'$ -dependent terms remain in the expression (these are the terms that control the efficiency of the CSA reintroduction). But for the S-CODEX experiment all possible $\omega_R t'$ -dependent terms remain,

$$-4 \begin{pmatrix} \sin(\omega_R t')(\sin \gamma + \cos \gamma) + \cos(\omega_R t')(\sin \gamma - \cos \gamma) \\ + \sin(2\omega_R t')(\sin 2\gamma + \cos 2\gamma) + \cos(2\omega_R t')(\sin 2\gamma - \cos 2\gamma) \\ - \sin \gamma + \cos \gamma - \sin 2\gamma + \cos 2\gamma \end{pmatrix} \quad (7)$$

the $\omega_R t'$ -dependent SIN terms cancel for the CONTRA sequence:

$$-4 \begin{pmatrix} \cos(\omega_R t')(\sin \gamma - \cos \gamma) + \cos(2\omega_R t')(\sin 2\gamma - \cos 2\gamma) \\ - \sin \gamma + \cos \gamma - \sin 2\gamma + \cos 2\gamma \end{pmatrix} \quad (8)$$

The consequences of the differences found between Eqs. (7) and (8) will be briefly discussed below.

Another comment appears to be in order: when examining the two different building blocks of the CSA recoupling periods, it becomes obvious that CONTRA refocuses the evolution due to the isotropic chemical shift while S-CODEX does not do so. In the ideal case, this does not have an influence, since the complete sequence consists of two such CSA recoupling blocks, one before and one after the mixing period and the pulse-phase setting makes sure that the phase accumulated by the isotropic chemical shift is canceled. However, the effect of pulse imperfections might lead to a mismatch that results in a deteriorated performance of the S-CODEX. Moreover, the refocusing of isotropic chemical shifts within each two rotor period block in CONTRA makes it possible to distinguish molecular processes that do not alter the isotropic chemical shift

(say, type A) from those that do (type B). As was discussed in the Results and discussion, section C of [6]: there will be a remaining dephasing of the lines in the acquired spectra for type A motion in S-CODEX but no dephasing in CONTRA data. This is similar to the comparison between trODESSA and CODEX for which the trODESSA permits this distinction too, while the Hahn-echo pulses in CODEX hide this information by refocusing the isotropic chemical shift during each of the recoupling periods.

4. Effects of pulse imperfections

One of the ideas upon introducing the new modifications in the S-CODEX sequence making it more symmetric with respect to the Hahn-echo π pulses might be reducing the effects of pulse imperfections. To confirm this assumption, we ran SIMPSON [19] simulations of the experiments. Since to our knowledge SIMPSON does not include exchange processes (yet), we set up dummy sequences that contain only the CSA recoupling cycles, as shown in Figs. 1b and c. The starting operator at $t = 0$ was chosen as I_X , the MAS rate was 10 kHz, and data were acquired at $t = 2 \cdot T_R$. The spin system was chosen to include a single ^{13}C nucleus with the magnetic parameters of the DMS molecule. Neither dipolar decoupling nor any phase cycling was applied.

In Fig. 2 a plot of the intensity of the first point of the FID, acquired at $t = 2 \cdot T_R$, versus t/T_R for different rf amplitudes of the π pulses is shown. The amplitude, A , was calculated from the real and imaginary parts of the first data point of the time-domain signal, i.e. $A = \sqrt{\text{real}(t=0)^2 + \text{imag}(t=0)^2}$. The ideal case was calculated assuming ideal pulses (δ pulses). It can be seen from the amplitudes $A(t_1)$ that S-CODEX is slightly more sensitive to finite-pulse artefacts when compared to CONTRA, however, the differences appear to be small. A much clearer presentation of this effect is depicted in Fig. 2c and d, where normalized difference amplitudes, $[A^{\text{ideal}}(t_1) - A^{\text{finite}}(t_1)]/A^{\text{ideal}}(t_1)$, are plotted versus t_1 for several finite rf powers with respect to the ideal case as shown for the amplitudes $A(t_1)$. Clearly, the effect of finite pulse length on S-CODEX (left) is more severe than on CONTRA (right), except for the value $t_1 = T_R/2$ where both experiments naturally coincide. Having confirmed our initial assumption, we went ahead to see how this appears in the real experimental data. Please note that the data for S-CODEX in Fig. 2 start only at $t_1 = 0.1 \cdot T_R$, in order to avoid pulse overlap of the second and third pulse for $t_1 = 0.05 \cdot T_R$. Interestingly, no dependence on the rf power was found in the CONTRA data for an evolution time $t_1 = 0.15 \cdot T_R$ (Fig. 2d). We will explore this effect in a later contribution.

5. Results and discussion

In this section, we will demonstrate the application of CONTRA using three samples: (i) DMS, a model substance that exhibits a well-defined two-site jump process and is fre-

Table 1
Pulse-timing parameters t and t^* for CODEX, S-CODEX and CONTRA experiments

	CODEX	S-CODEX	CONTRA
t	$T_R/2$	t_1	t_1
t^*	$3 T_R/2$	$T_R + t_1$	$2 T_R - t_1$

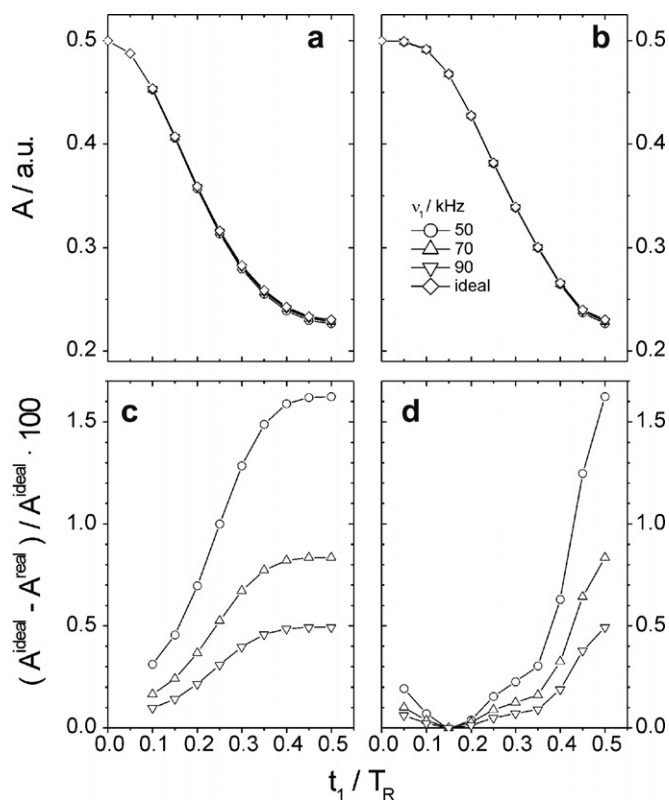


Fig. 2. SIMPSON simulations of the finite pulse effect length on the CSA recoupling for (a) S-CODEX and (b) CONTRA dummy experiments for different v_1 values, as indicated. The amplitude values, A , are calculated from the 1st points of the calculated FID acquired at $t = 2 \cdot T_R$, as described in the text. (c and d) SIMPSON plots of the normalized amplitude difference, calculated from the data shown (a and b). The data are the difference of the Amplitude values for different finite rf powers, normalized to the data at infinite power (ideal case).

quently used to test methods aimed to slow molecular dynamic processes; (ii) the amorphous polymer PMMA, an example for a bimodal process, where the carbonyl group that serves as a linker between the main and side chain undergoes two different simultaneous processes that have been already characterized by static ^{13}C -2D and 1D-exchange NMR before [20–23] and (iii) a sugar glass, where the carbohydrate molecules are in the amorphous state, being an example for a poorly defined process about which no prior knowledge from other experiments exists.

6. DMS

DMS is a popular test sample (for a compilation see [24]) that exhibits—besides having convenient magnetic and kinetic parameters—a well-defined molecular process, namely a two-site jump with a single-exponential correlation function of motion. Fig. 3a shows the dependence of the CONTRA-dephasing curve $(S_0 - S)/S_0 = \Delta S/S_0$, calculated using the magnetic parameters of the DMS molecules in the limit $\tau_c \ll t_m$, and for different (hypothetical) jump angles (the DMS molecule corresponds to 54°). S and S_0 being is the signal intensities of the exchange and reference experiments. It is obvious that the CONTRA

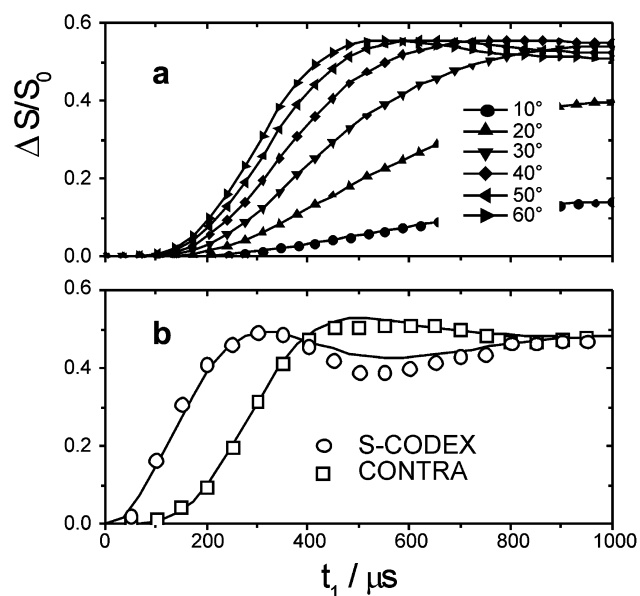


Fig. 3. Calculated data for a 2-site jump motion, using the equations given in the text and magnetic parameters of the DMS molecule ($\sigma_i = 19.75, 19.75, -39.5$ ppm) and a rotation around the Euler angle β . MAS rate = 4 kHz and $N = 4$. (a) CONTRA data for the effect of different jump angles $\pm\beta$. (b) Experimental and calculated S-CODEX and CONTRA data for $\beta = \pm 54^\circ$, fitting the DMS molecule. The S-CODEX data and calculation is given for comparison, also. Note the mismatch between experiment and calculation for the latter at t_1 values between 400 and 800 μs which almost does not appear for the CONTRA data.

curves resemble a behavior comparable to those of the S-CODEX, namely a faster increase towards the asymptotic plateau for larger jump angles, i.e. it provides basically the same dynamic information. More interesting, however, is the comparison of the S-CODEX and CONTRA-dephasing curves for a given jump angle, Fig. 3b. As can be seen, the CONTRA curve starts for short t_1 values almost horizontally at the value $\Delta S/S_0 \approx 0$. This has some advantages since the early data points suffer most from artefacts due to the finite π -pulse length, an effect that can be seen, for example, in Figs. 10 and 11 of [16]. For the CONTRA, one can safely assign the value $\Delta S/S_0 \approx 0$ to these data points. This fortunate behavior is a consequence of the remaining COS terms in Eq. (8), as compared to Eq. (7).

Fig. 3b compares calculated and experimental S-CODEX and CONTRA data for DMS. The experimental data were scaled to account for the finite t_m such that the value of the asymptotic plateau is 0.47, rather than 0.5. One can see that the agreement between experiment and simulation is excellent. After careful examination of this figure it can be seen that there is a small deviation in the range $t_1 = 500 \dots 600 \mu\text{s}$ between the simulated and experimental S-CODEX data (the reason of which still remains unknown). Such deviations do not occur for the CONTRA data.

7. PMMA and sugar glass

A more challenging example is the study of the PMMA side chain β relaxation, shown in Fig. 4. The carbonyl

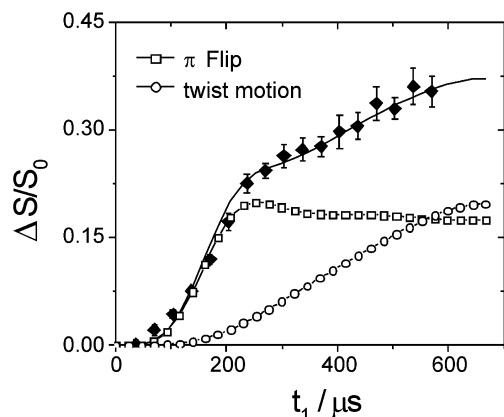


Fig. 4. Experimental (full symbols) and calculated data (open symbols, full line) for the PMMA COO group. $T = 25^\circ\text{C}$, MAS rate = 6 kHz. The dynamic process consists of a large-angle π -flip and a superposed small-angle twist motion. For details, see [22,23,25]. The solid line through the experimental data is the sum of the calculated points.

group of the amorphous polymer poly-(methyl methacrylate), PMMA, performs a π -flip around the C–COO bond, which is accompanied by a small-angle twist motion of the local backbone segment [25]. In terms of the jump geometry, this means a superposition of a large-angle motion (flip) and a small-angle reorientation (twist). Due to the large value of the carbonyl group CSA of about 150 ppm, it is difficult to acquire the early data points for the flip motion by conventional CODEX. In fact, one has to work at MAS speeds beyond 10 kHz, which in turn might create problems with the stability and, in particular, with the calibration and stability of the sample temperature. In more sensitive samples, the different centrifugal forces might even alter the physical state of the material. Using CONTRA, as shown in Fig. 1c, it is simple to acquire the entire dynamic dephasing/evolution curve in a constant time and constant MAS-rate manner. Fig. 4 shows the experimental data together with the calculated curve that is composed from the superposition of the flip and the twist motions. It is worth mentioning that the CONTRA signal does not need to be acquired with equidistant t_1 values. Any array of t_1 values can be used and thus, for example, the data points could be chosen densely in the t_1 range where the flip motion is almost uniquely well characterized (small t_1 values), and less densely for the remaining t_1 values, saving precious machine time.

Similarly, Fig. 5 shows experimental and simulated CONTRA data for OCH₃ carbons in amorphous methyl rhamnose. From the comparison of the experimental data with calculations based on single jump angles it became clear that the actual process must be more complex. Manual superpositions of calculated CONTRA data for different models such as a bimodal jump-angle distribution or a log-Gaussian distribution of jump angles were compared. The results suggested that these carbons experience twofold dynamics, namely partial the chair–chair interconversion of the ring and an additional small-angle motion around

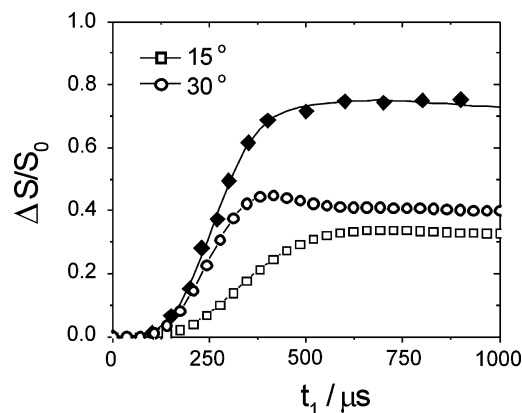


Fig. 5. Experimental (full symbols) and calculated data (open symbols, full lines) for the OCH₃ (top) and CH₃ (bottom) groups in methyl rhamnose glass. The experimental data are explained by superposition of flips by 15° and 30° , respectively. Each flip contributes about half to the motion. This indicates the high sensitivity of the method to the amplitude of small-angle jumps. For details, see [16]. $T = 15^\circ\text{C}$, MAS rate = 4 kHz. The solid line through the experimental data is the weighted sum of the calculated points.

the C–O–C bonds by the OCH₃ group itself [16]. Although a quantitative processing was possible, the data of the original work clearly show the artefacts as discussed above, while the CONTRA data shown in Fig. 5 does not. The simulated curves are calculated using the same parameters as in [16].

8. Conclusions

We presented a minor but essential modification to a previously introduced modification of the CODEX experiment. It permits the running experiments aimed to extract data for the amplitude of molecular dynamic processes at a constant time and constant MAS-spinning rate manner and thus, avoid problems related with matching data obtained at different experimental conditions. It is also has advantages over the version introduced previously, being less sensitive to artefacts caused by the finite length of the rf pulses.

Acknowledgments

We acknowledge financial support from the Deutsche Forschungsgemeinschaft DFG in the framework of Sonderforschungsbereich SFB 418. D.R. acknowledges financial aid from the Deutscher Akademischer Austauschdienst DAAD. E.R.dA and T.J.B. thanks FAPESP, CNPq and CAPES for financial support. A.S. acknowledges the support of the Israel Science Foundation founded by The Israel Academy of Sciences and Humanities. We are indebted to Anja and Christiane for help in inventing the acronym. This work was powered by Brazilian coffee.

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