We are extremely grateful to the reviewer for her/his time and effort in reviewing the manuscript. We apologize for the unclear description of the main ideas of the article. It is true that there is not a single focus to this article, however, we believe it does not make any sense to split this into multiple parts. We hope that the following explanations below will convince the reviewer that what he/she refers to as 'wrong' is in fact correct but lacked sufficient explanation. While we could likely have published an article on heteronuclear RFDR alone, we feel that the more complete article will better serve the solid-state NMR community.

The paper by Nimerovsky and coworker describes fp RFDR applied to homonuclear and heteronuclear coupled dipolar spin systems.
My first impression after reading the manuscript was, that there is no clear focus and clear message of the paper draft. Is the main message a theoretical framework to analyze such sequences (in this case, it is not clear to me what is new)…

The main goal of the article is to show a theoretical interpretation of the fp-RFDR sequence and the mechanisms with which the fp-RFDR signal is transferred between the spins. We analyze the fp-RFDR sequence using numerical code written by us. The main conclusions are:

1. The heteronuclear and homonuclear transferred fp-RFDR signals can be obtained with the same exactly sequence. For the homonuclear spin system the transfer is described by I_{zk} $\xrightarrow{fp-RFDR} I_{zp}$, whereas for the heteronuclear spin system the transfer is described by I_z $\xrightarrow{fp-RFDR} S_z$. The heteronuclear fp-RFDR transfer has not been described before.

2. The heteronuclear and homonuclear transferred signals coincide completely at the time points of whole number of rotor periods, if the ratio between values of the heteronuclear ($\nu_{D,IS}$) and homonuclear ($\nu_{D,IkIp}$) dipolar coupling constants are 1.5 and the differences between offset values of the spins (Ω_{IS} for heteronuclear case and Ω_{IkIp} for homonuclear case) are significantly smaller with respect to the used MAS rate (ν_R): $\frac{\Omega_{IS}}{\nu_R} \ll 1$ and $\frac{\Omega_{IkIp}}{\nu_R} \ll 1$. These conditions are firstly demonstrated in this article.

3. The heteronuclear and homonuclear transferred signals can be described with the same model Hamiltonian, if the conditions, $\frac{\Omega_{IS}}{\nu_R} \ll 1$ and $\frac{\Omega_{IkIp}}{\nu_R} \ll 1$, are met and the measurements occurs every whole number of rotor periods. It does not mean that this model Hamiltonian describes the evolutions of the heteronuclear and homonuclear spin systems correctly at every time point of the transfer, which is shown in the article. The model Hamiltonians are indeed not correct for arbitrary conditions, but are useful under the conditions described in the article. Their use is firstly demonstrated in this article.

4. XY phase cycling plays a crucial role in the fp-RFDR transfer. With XX phase cycling the fp-RFDR transfer is always zero at the time points of whole number of rotor periods for both homonuclear and heteronuclear spin system (under condition that $\Omega_{IS} = 0$ and $\Omega_{IkIp} = 0$). We show it with the numerical simulations and provide the theoretical proof for I_2 homonuclear spin system using fictitious half spin formalism[1]. This conclusion is opposite with respect to the traditional statement in which the role of XY phase cycling was mentioned as the secondary[2] and fp-RFDR transfer could be achieved with any phase cycling[3]. The crucial role of XY phase cycling in the fp-RFDR transfer is firstly demonstrated in the article.

5. The presence of the offset difference not only has an influence on the efficiency of the transfer, it changes the mechanism of the transfer. It was shown with the model Hamiltonians,

since under different simulated conditions we used different model Hamiltonians. This idea is consistent with AHT literature that demonstrates 2 mechanisms for RFDR.

6. Investigating the evolution of the IS and I_2 spin system during two rotor periods we show the paths with which the heteronuclear and homonuclear fp-RFDR signals are transferred. The fp-RFDR signals for both spin systems are manly transferred via mix of Double and Zero Quantum terms. If for IS spin system, only one path is used for transfer the signal: $I_z \rightarrow I_x S_y \rightarrow S_z$, the homonuclear transferred signal uses 64 paths. Despite such huge difference of the evolutions during these two rotor periods, the amplitudes of the operators in the end of two rotor periods coincide completely. The next Fig. shows the schematic illustration of these paths (this Fig. was prepared as a graphical abstract). These paths are firstly demonstrated in this article.

Heteronuclear fpRFDR path **Homonuclear fpRFDR paths**
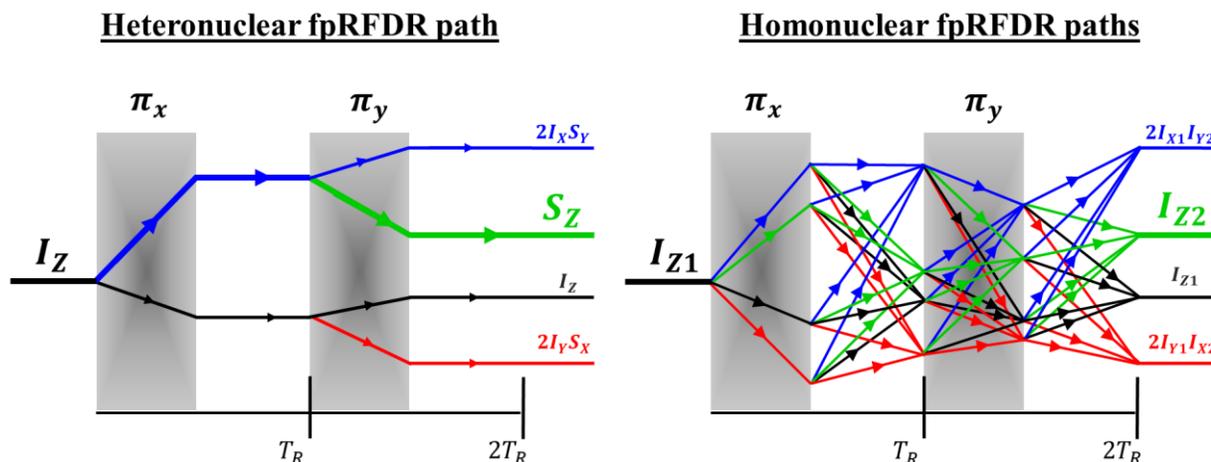
The fp-RFDR paths for heteronuclear IS (left) and homonuclear I_2 (right) spin systems during first two rotor periods.

…or is it the use of simultaneous RFDR-like sequences on heteronuclear spins systems to achieve heteronuclear polarization transfer.

The fp-RFDR sequence was used without any modifications. For the theoretical description only the internal Hamiltonian indicates if the homonuclear or the heteronuclear spin system is considered. With respect to rf-field Hamiltonian, there is no any difference if we apply a train of π-pulses on N homonuclear ½ spins or we apply a train of π-pulses on N heteronuclear ½ spins.

The second point is that the theory part and the first part of the simulations part seems to be very much detached and unconnected to the main part of the paper. I must admit that the manuscript left me a bit at a loss how things are connected and what the authors want to tell.

In the "Theory" section we explain how the numerical simulations were performed. We used the equation of motion (the Liovuille-von Neumann equation, Eq. 1.1 in the article, page 5) to calculate the evolutions of the spin operators (Eq. 1.3 in the article, page 5). To deal with the Dyson operator, we split two propagators between 0 and t_p (during the pulse) and between t_p and T_R (during the delay) on N sub-propagators each. After the analytical integration each of these sub-propagators were diagonalized. This idea was firstly implemented on IS spin system, where S spin was 3/2 spin with a large quadrupolar coupling interaction[4]. We will add a sentence to the revised article that: "*This section describes how our numerical simulations were performed.*".

The theory part is quite lengthy and discusses the details of time slicing used in numerical simulations. There is nothing new in this part and it could be left away with any loss of information.

We agree that this section shows nothing new. We emphasize it in that section, page 5, lines 112-113: "*This is the way that calculations are performed in the popular SIMPSON software*". However, we still have to explain how our numerical calculations were performed. In particular, most journals encourage providing a level of detail that allows the reproduction of results independent of other published literature.

But since it is here, I was wondering about two things: (1) Why is the pulse and the remaining rotor period divided into an equal number of time slices. Typically, one would implement time slicing such that the rotor period is divided into a certain number of slices and the pulse occupies whatever time it takes. Here it says explicitly: "The numerical calculations split each of these two parts into N sub parts with the lengths tp/N and (TR – tp)/N, respectively." If SIMPSON was used for the simulations, this is most likely not correct. And why would one do this and have a higher sampling rate during the pulse?

The numerical simulations were performed with our own written programs. For some simulations we used ultra-fast MAS of 90 kHz (page 10, Fig. 4 and page 29 Fig. A1c-d). In that cases the duty factor was significantly increased. Therefore, we used the same N value for both these periods of time to keep it as a constant under different simulated conditions. We agree that the slicing could be done in more sophisticated way. However, the result would be the same.

(2) Eq. (2.4) is only correct if the Hamiltonian H(t) commutes with itself over the time period Delta of the integration. This is however not how numerical simulations are typically implemented when doing time slicing. Usually, it is assumed that the Hamiltonian is constant over the time interval used for the calculations and I am pretty sure that this is how SIMPSON implements it. I think the statements and the equation at the end of page 5 are wrong.

We assume that reviewer refers to Eq.(1.4). We agree that in SIMPSON simulations the Hamiltonian is assumed as a constant over the time interval, which is a kind of numerical integration. It was mentioned in the article (page 5, lines 113-116): "*The main difference in our implementation of numerical evolutions with respect to SIMSPON calculations is to use analytical integrations over a small slice rather than numerical integrations...*".

However we agree that the last part of this sentence is not correct for this specific situation (…", *which significantly reduces the computer time*."), and it is removed.

In the simulation part, first different approximations for the Hamiltonian are used to understand which part of it is responsible for the polarization transfer under different conditions. The Hamiltonian of Eq. 2.1 makes sense (full rotating-frame truncated dipolar Hamiltonian) but it would be nice to rewrite the second part with 2zz instead of 3zz-zz but the ones selected in Eq. 2.2 do not really make sense or are wrong. The zz only Hamiltonian should have a coefficient of 1 and not 1.5! The second one is a J coupling Hamiltonian which makes no sense in this context while the third one is the ZQ part which is sensible. If these are indeed the Hamiltonians used for the simulations, I would put a big question mark on the conclusions presented in Figs. 3- 5. This is implied in the figure labeling but of course I cannot judge what was used in the simulations.

We did not try to convince that the model Hamiltonians, Eq. (2.2b-c) could show which part of the full high field truncated Hamiltonian "was responsible for the polarization transfer under different

conditions". The full Hamiltonian was used for simulations, unless noted. The goal of the model Hamiltonians was mentioned on the page 7, lines 152-154: "*Firstly we investigate which part of the full high field dipolar Hamiltonian can be a model Hamiltonian. A model Hamiltonian is a simplified Hamiltonian, which provides the same evolution of the spin system at specific time points as a full dipolar Hamiltonian.*".

However, we agree that a sentence in the end of the previous section was unclear (page 7, lines 137-138): "*We investigate the influence of each part of the Dipolar Hamiltonian (the secular and the flip-flop parts) on the measured operators at specific time points under different simulated conditions.*" We apologize for it. We modified this sentence (page 7, lines 137-138 in the revised article): "*We investigate the behavior of the measured operators at specific time points under different simulated conditions, by separately analyzing different parts of the full high field truncated Dipolar Hamiltonian (the secular and the flip-flop parts).*"

Eqs.(2.2a-c) (page 7, lines 155-156) represent the model Hamiltonians. Using the model Hamiltonian we cannot make any conclusions about the model Hamiltonian itself, but the evolutions of the operators at specific points. Under conditions when the differences between offset values of the spins significantly smaller with respect to the used MAS rate, the model Hamiltonian (2.2a) provides the same evolutions of the operators as with the full high field truncated Hamiltonian (Eq. 2.1). It is shown on Figs. (2a and 4a). Under conditions when the differences between offset values of the spins is not small with respect to the used MAS rate, the model Hamiltonian (Eq. 2.2c) provides the same evolutions of the operators at specific time points as with the full high field truncated Hamiltonian (Eq. 2.1), which is shown in Fig. 3b. The model Hamiltonian Eq. (2.2b) was used as a part of the investigation.

On page 11, the heteronuclear Hamiltonian is discussed: "The main difference to the heteronuclear full dipolar Hamiltonian with a homonuclear model Hamiltonian (Eq. 2.1a) is a factor of 1.5." This is clearly not correct. The heteronuclear Hamiltonian has just the zz terms and is exactly the same as a homonuclear (weakcoupling) dipolar Hamiltonian. There is no factor of 1.5 difference between the two. Where we can find a factor of 1.5 is in the transition frequencies after diagonalisation. All these statements that are clearly wrong make me worry about the results presented in this paper.

A model Hamiltonian is a simplified Hamiltonian, which provides the same evolution of the spin system at specific time points as a full dipolar Hamiltonian. Eq. (2.2a) has the same structure as a full high field truncated heteronuclear dipolar Hamiltonian. The difference is a factor 1.5. In our simulations when we compared the evolution of the homonuclear and heteronuclear spin systems, we kept the ratio between homonuclear and the heteronuclear dipolar coupling values as 1:1.5 (Figs. 5-7). Under this condition and the negligible small difference of the offset values of the spins the heteronuclear and homonuclear fp-RFDR signals completely coincide at whole number of rotor periods. We used the model Hamiltonians only to make Figs. 2-4. For all other Figs. the full dipolar Hamiltonian was applied. We will add the sentence about it. We also will add to the captions of Figs. 5-9 that: "*The full dipolar Hamiltonian (Eq. 2.1) was used to evaluate the I_2 spin system and the secular Hamiltonian was used to evaluate IS spin system.*"

There is another statement that worries me (page 13): "For negligible offset differences with respect to the MAS rate, the evolution of the operators of IS and I2 spin systems are the same at specific time points." What are negligible offset differences in a heteronuclear spin system when the two spins are in different rotating frames? And further on: "With increase of offset difference the IS spin system passes through specific rotor resonance condition (the difference between offsets equal to half of the MAS rate), under which the transfer does not occur. For the I2 spin system the velocity of the transfer increases with increased offset difference." This cannot be. Either the authors mix up homo- and

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heteronuclear spin systems or this is plain wrong. There are no MAS resonance conditions in heteronuclear spin systems that depend on any offsets (what offset differences are there?).

For I_2 spin system the applied internal Hamiltonian was:
$$H = \Omega_{I1}I_{z1} + \Omega_{I2}I_{z2} + 0.5\omega_{D,II}(t)[3I_{z1}I_{z2} - \bar{I}_1\bar{I}_2], \quad \text{Eq. (R1)}$$
whereas the heteronuclear internal Hamiltonian was:
$$H = \Omega_I I_z + \Omega_S S_z + \omega_{D,IS}(t)I_z S_z. \quad\quad\quad\quad \text{Eq. (R2)}$$
The offset difference was meant as $|\Omega_I - \Omega_S|$ for heteronuclear and $|\Omega_{I1} - \Omega_{I2}|$ homonuclear spin systems. Although an offset difference for the heteronuclear case may seem irrelevant when each spin is in a different rotating frame (as was noticed by reviewer), it can be seen from Eqns R1-2 that the offsets appear with the same mathematical form. The appearance of a resonance condition is perhaps less surprising when considering that essentially identical RF pulsing is applied on both channels by design of the pulse sequence. Fig. 5c (page 14) shows the case when the transfer between the operator I_z and S_z has negligible small value. It occurs when $|\Omega_I - \Omega_S| = 0.5\omega_R$ and the heteronuclear dipolar coupling is smaller with respect to MAS rate. Since we are first who show the heteronuclear fp-RFDR transfer, such "rotor resonance condition" has never been mentioned. The same results and conclusions can be obtained with SIMSPON simulations. Some SIMPSON codes for I_2 and IS spin systems under different simulated conditions are shown in the end of this response.

Even if some of the problems are just a mix up, all of these mistakes make me wonder how carefull the rest of the work is done. I have not and will not look at the rest of the manuscript before all these problems are corrected or explained.

We hope that after these clarifications, the reviewer will continue to review our article. This manuscript has been prepared with a great deal of care, and simulation results have been checked against SIMPSON.

Some minor remarks that should be cleaned up:

(1) The introduction has a long list of references to homonuclear and heteronuclear recoupling experiments that is clearly incomplete. Instead of such an incomplete list, it would be much better to have a reference to a review. There is for example a recent review about dipolar resoupling by N.C. Nielsen, L.A. Strassø, A.B. Nielsen, (Top. Curr. Chem. 306 (2012) 1–45) as well as older reviews on his topic. I think it would be more appropriate as a reference than an incomplete list.

We will include that review into citation. We have made no attempt to provide a complete list of recoupling experiments and hope the reviewer can forgive omission of any particularly relevant literature.

2) page 5 line 99/100: Liovuille-von Neumann equation is much more common. Why hbar=1? Usually the Hamiltonian in NMR is in frequency units and then there is no hbar in front of the commutator.

We removed $\hbar$ and mentioned Eq. (1.1) as an equation of motion.

(3) Equation numbering should be continuous from (1) to (N) without chapter subdivisions.

We will modify all equation numbering according to this suggestion.

We prepared three different SIMPSON codes, representing I_2 (code 1) and IS (codes 2 and 3) fp-RFDR sequences. The transferred signals with codes 1 and 2 coincide completely, since all spins are on-

resonance and the ratio between the heteronuclear and homonuclear dipolar coupling constants is 1.5. The code 3 represents the case, when the difference between offsets of the heteronuclear spins is half of MAS rate and the dipolar coupling constant is smaller with respect to MAS rate. The transferred fp-RFDR signal is negligibly small.

Code 1

```
spinsys {
 channels 1H
 nuclei   1H 1H
 dipole 1 2 -2e3 0 0 0
}

par {
 proton_frequency 600e6
 spin_rate      10000
 sw           spin_rate/8
 np           20
 crystal_file    rep100
 gamma_angles    14
 start_operator   I1z
 detect_operator  I2z
 verbose        1101
 variable rfq    50000
}
proc pulseq {} {
 global par

 maxdt 1

 set t180 [expr 0.5e6/$par(rfq)]
 set DELAY [expr (1e6/$par(spin_rate))-$t180]

 reset
 pulse $t180 $par(rfq) x
 delay $DELAY
 pulse $t180 $par(rfq) y
 delay $DELAY
 pulse $t180 $par(rfq) x
 delay $DELAY
 pulse $t180 $par(rfq) y
 delay $DELAY
 pulse $t180 $par(rfq) y
 delay $DELAY
 pulse $t180 $par(rfq) x
 delay $DELAY
 pulse $t180 $par(rfq) y
 delay $DELAY
 pulse $t180 $par(rfq) x
 delay $DELAY

 store 1
```

6

```
  reset
  acq
  reset

  for {set i 1} {$i <$par(np)} {incr i} {
  prop 1
  acq
  }
}

proc main {} {
  global par

  set   f [fsimpson]
  fsave $f $par(name).fid
  fsave $f $par(name).dat -xreim
}
```

```
spinsys {
  channels 1H 13C
  nuclei   1H 13C
  dipole 1 2 -3e3 0 0 0
  shift  1 0e3 0 0 0 0 0
  shift  2 0e3 0 0 0 0 0
}

par {
  proton_frequency 600e6
  spin_rate      10000
  sw             spin_rate/8
  np             20
  crystal_file   rep100
  gamma_angles   14
  start_operator  I1z
  detect_operator  I2z
  verbose        1101
  variable rfq   50000
}
proc pulseq {} {
  global par

  maxdt 1

  set t180 [expr 0.5e6/$par(rfq)]
  set DELAY [expr (1e6/$par(spin_rate))-$t180]

  reset
  pulse $t180 $par(rfq) x   $par(rfq) x
  delay $DELAY
  pulse $t180 $par(rfq) y  $par(rfq) y
  delay $DELAY
  pulse $t180 $par(rfq) x   $par(rfq) x
  delay $DELAY
  pulse $t180 $par(rfq) y  $par(rfq) y
```

```
    delay $DELAY
    pulse $t180 $par(rfq) y  $par(rfq) y
    delay $DELAY
    pulse $t180 $par(rfq) x  $par(rfq) x
    delay $DELAY
    pulse $t180 $par(rfq) y  $par(rfq) y
    delay $DELAY
    pulse $t180 $par(rfq) x  $par(rfq) x
    delay $DELAY

    store 1
    reset
    acq
    reset

    for {set i 1} {$i <$par(np)} {incr i} {
    prop 1
    acq
    }
}

proc main {} {
  global par

  set   f [fsimpson]
  fsave $f $par(name).fid
  fsave $f $par(name).dat -xreim
}
```

Code 3   %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```
spinsys {
  channels 1H 13C
  nuclei   1H 13C
  dipole 1 2 -3e3 0 0 0
  shift  1 -2e3 0 0 0 0 0
  shift  2 3e3 0 0 0 0 0
}

par {
  proton_frequency 600e6
  spin_rate      10000
  sw             spin_rate/8
  np             20
  crystal_file   rep100
  gamma_angles   14
  start_operator  I1z
  detect_operator I2z
  verbose        1101
  variable rfq   50000
}
proc pulseq {} {
  global par

  maxdt 1
```

```
set t180 [expr 0.5e6/$par(rfq)]
set DELAY [expr (1e6/$par(spin_rate))-$t180]

reset
pulse $t180 $par(rfq) x   $par(rfq) x
delay $DELAY
pulse $t180 $par(rfq) y  $par(rfq) y
delay $DELAY
pulse $t180 $par(rfq) x   $par(rfq) x
delay $DELAY
pulse $t180 $par(rfq) y  $par(rfq) y
delay $DELAY
pulse $t180 $par(rfq) y   $par(rfq) y
delay $DELAY
pulse $t180 $par(rfq) x  $par(rfq) x
delay $DELAY
pulse $t180 $par(rfq) y   $par(rfq) y
delay $DELAY
pulse $t180 $par(rfq) x  $par(rfq) x
delay $DELAY

store 1
reset
acq
reset

for {set i 1} {$i <$par(np)} {incr i} {
prop 1
acq
}
}

proc main {} {
 global par

 set   f [fsimpson]
 fsave $f $par(name).fid
 fsave $f $par(name).dat -xreim
}
```

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