AN ANALYSIS OF DNP CROSS-TALK EXPERIMENTS FOR SEVERAL NUCLEI

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Introduction

Dynamic nuclear polarization (DNP) is an efficient and versatile method that enables one to increase signal intensity in nuclear magnetic resonance (NMR). Hyperpolarization of nuclear spins is achieved by transferring the high electron polarization to the former through microwave (mw) irradiation. Admittedly, this transfer is achieved through three main mechanisms, namely, the solid effect (SE) which involves forbidden electron-nuclear transitions, the cross effect (CE) and thermal mixing (TM).

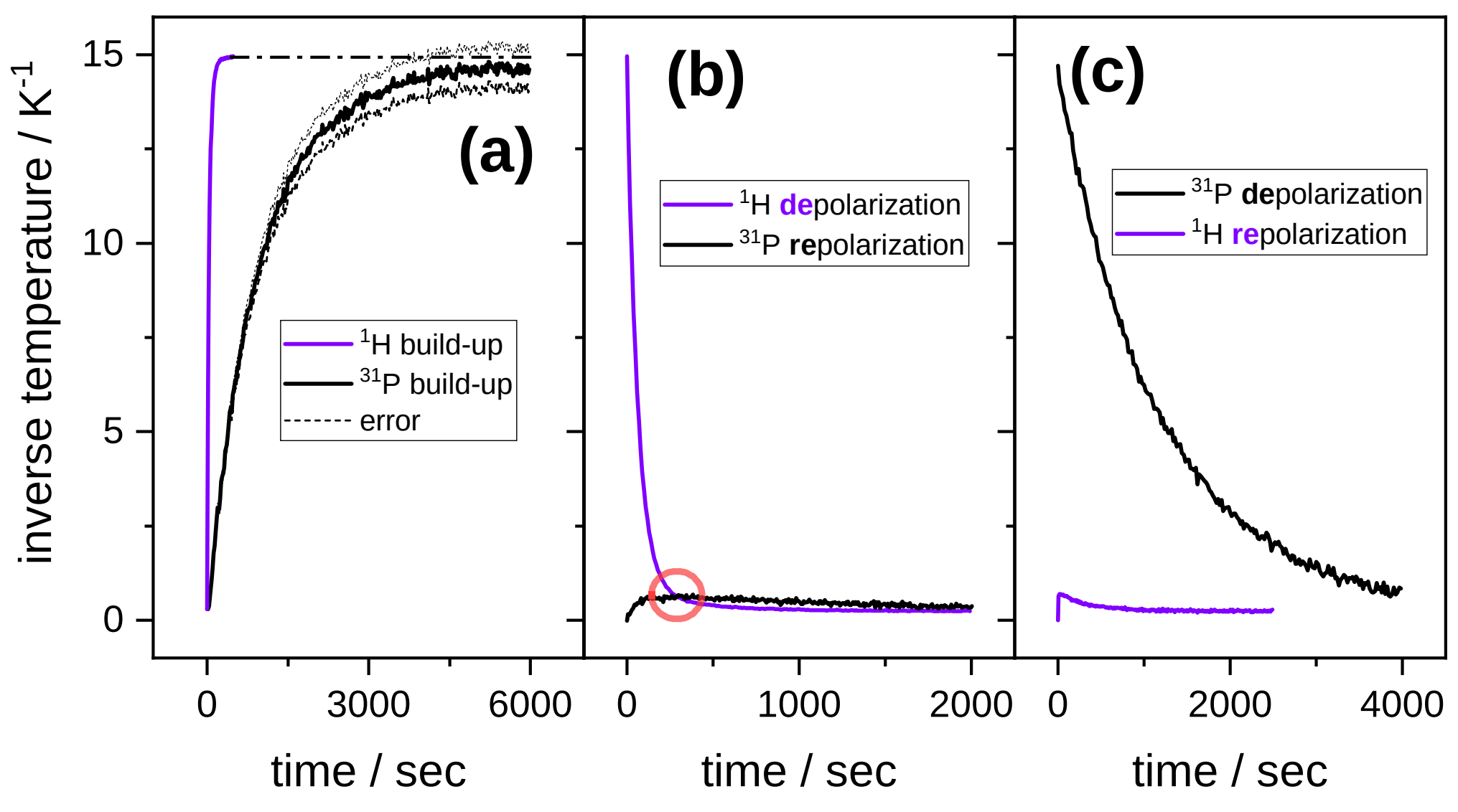

Figure 1: (a) build-up experiments for different nuclei reaching the same spin temperature, (b)-(c) depolarization and repolarization experiments for different nuclei

It was proposed that TM occurs when two conditions are met:

- both nuclei reach a common spin temperature under mw irradiation (fig 1a)
- both nuclei reach a common spin temperature (different from the lattice) when either of the nuclei is initially depolarized (fig 1b); this ramp of polarization is also known as cross-talk

The goal of this work is to numerically describe these curves and to extract parameters characterizing DNP juice in the TM conditions.

Theoretical model

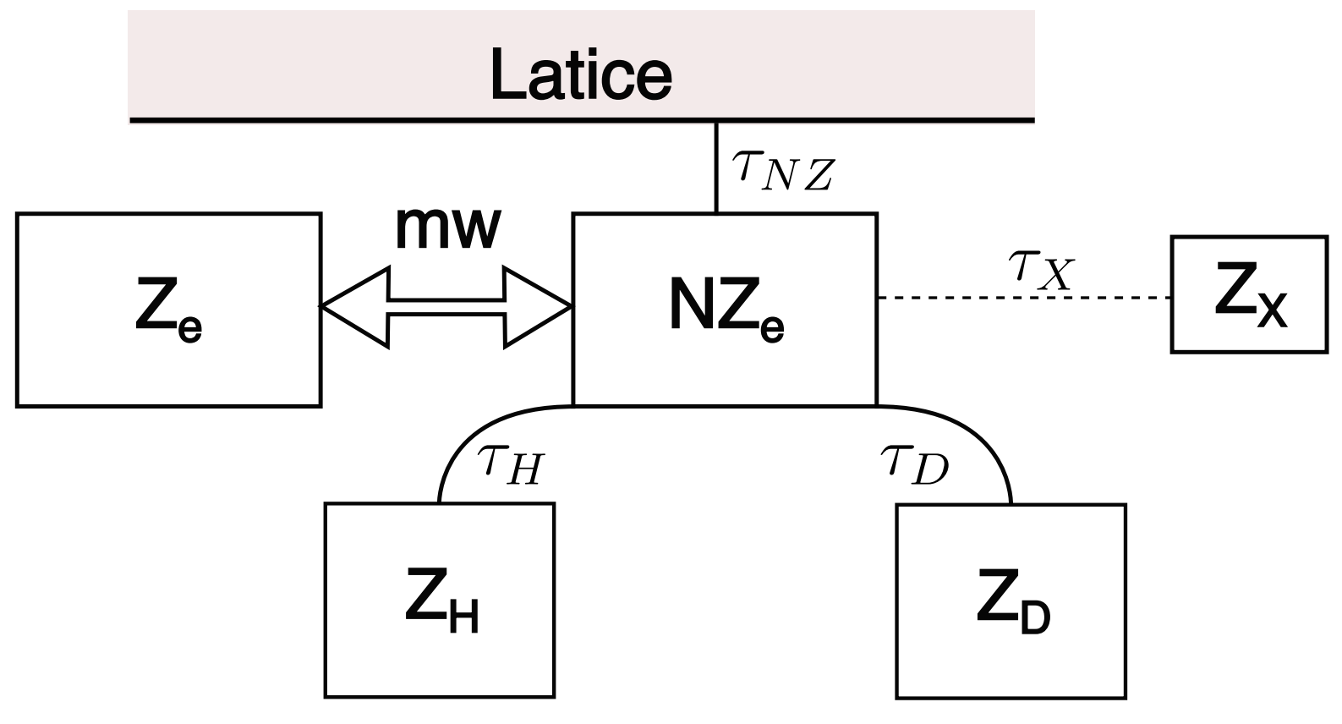

Figure 2: The interaction scheme for Provotorov's thermal mixing equations

It is common for TM regime to use Provotorov's equation. In case when the inner local relaxation is fast, one can factorize density matrix by using so called spin temperature: the temperature that should correspond to the obtained Boltzman distribution in the reservoir. Usually, two types of reservoir are distinguished:

- zeeman reservoir Z_i for electrons and nuclei
- non-Zeeman reservoir for electrons (NZ_e), with the main contribution being electron-electron interaction

mw irradtiation transfer energy from Z_e to NZ_e, where the energy is then transferred to the neighboring nuclei. The scheme is shown on figure 2. To numerically describe it, one can use the following equations:

$$\begin{gathered}\frac{d\beta_H}{dt} = -\frac{1}{\tau_H}\left(\beta_H - \beta_{NZ}\right), \qquad \frac{d\beta_D}{dt} = -\frac{1}{\tau_D}\left(\beta_D - \beta_{NZ}\right), \\ \frac{d\beta_{NZ}}{dt} = -\frac{c_H}{c_{NZ}}\frac{1}{\tau_H}\left(\beta_{NZ} - \beta_1\right) - \frac{c_D}{c_{NZ}}\frac{1}{\tau_D}\left(\beta_{NZ} - \beta_D\right) - \frac{1}{\tau_{NZ}}\left(\beta_{NZ} - \beta_L\right)\end{gathered} \tag{1}$$

where τ_i is the interaction time constant, and the $c_{H,D}$ and c_{NZ} are nuclear Zeeman and electron non-Zeeman heat capacities, defined as:

$$c_i = \frac{n_i\left(\gamma_i B\right)^2 I(I+1)}{3}, \quad c_{NZ} = \frac{n_e \Delta^2 I(I+1)}{3}, \tag{2}$$

here Δ is the width of an EPR line. **By knowing that the spin temperatures for HD are equal, we can suppose that NZ reservoir has the same temperature**.

HD cross-talk

The cross-talk properties is very pronounced on the H curves in the DNP juice. One can see that even during depolarization experiment on fig 3a, where the decaying curve shows either bi or monoexponential decay depending on the D saturation. The repolarization experiments show even bigger difference (3b). One can see the decay is much faster with D saturation. By direct fitting it may reveled that the slow decay corresponds to the D decay.

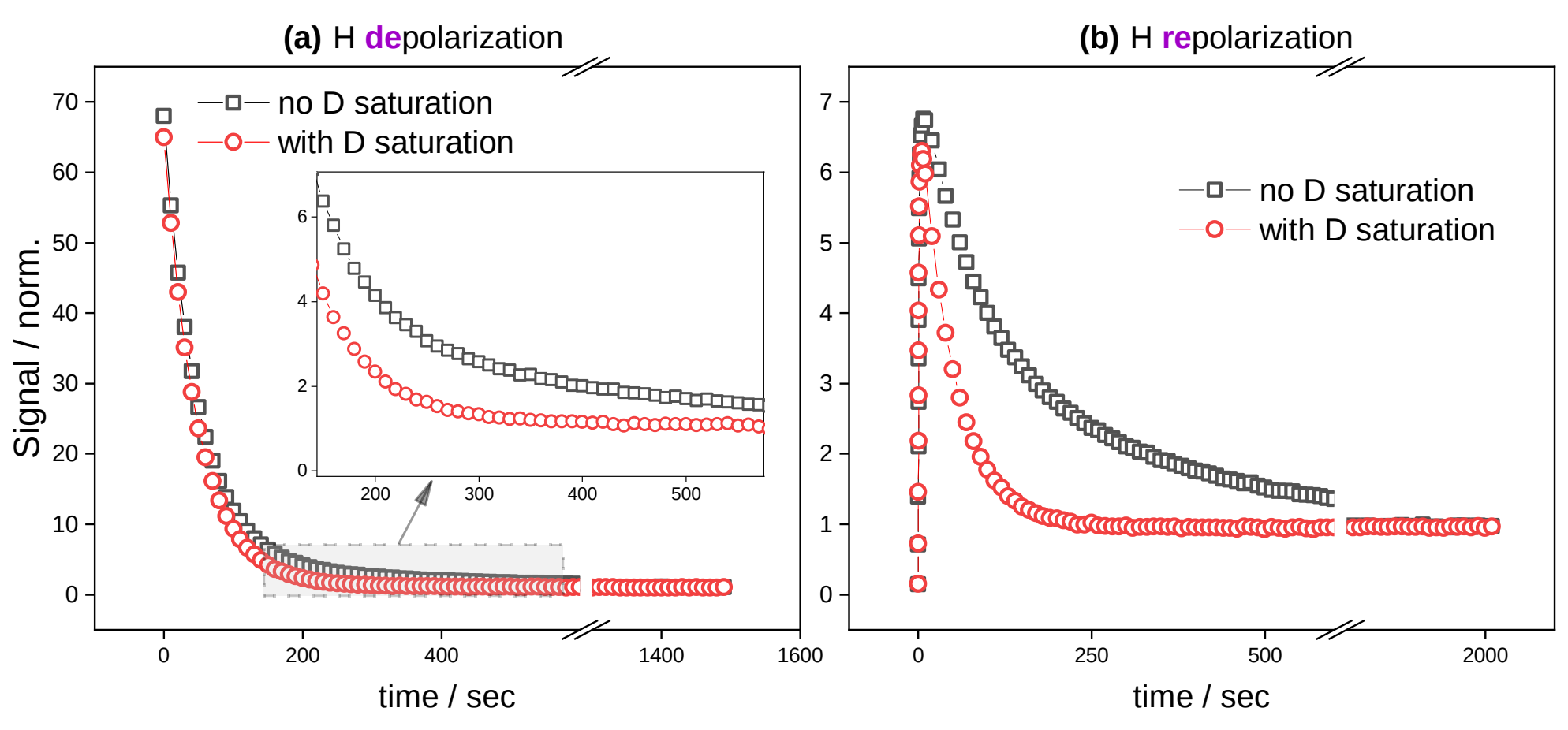

Figure 3: (a) depolarization and (b) repolarization H experiments with different D initial states

The fact that H curves already contain the information on D, it allows one to fit only H data with D manipulation. Nevertheless, for consistency the whole fit of HD data is shown hereafter.

Conclusions

Knowing two sets of H data it is possible to simulate the properties of DNP-juice in the TM regime, allowing one to simulate any possible X-nuclei, or analyse the obtained parameters in general. Varying TEMPOL and H/D concentration, we find clear existence of the both close and bulk hidden spins.

Fitting result

Here is an example of the one fit set for 60 mM TEMPOL 10/40/50 H_2O/D_2O/glycerol-d8 DNP sample:

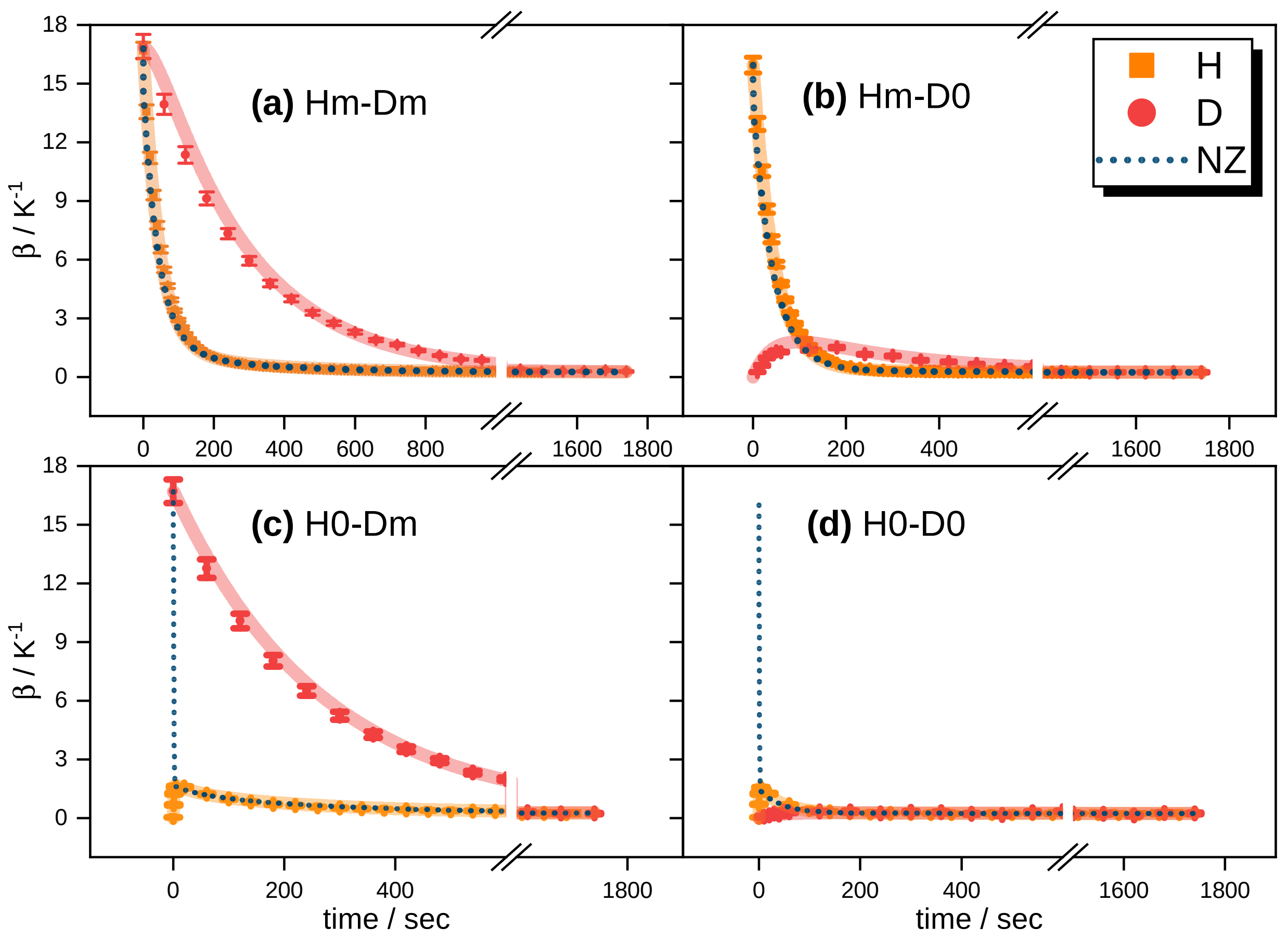

Figure 4: The overall HD fit. For every experiments from (a)-(d) initial condition differs: nuclei can be either polarizaed or depolarized

It seems like the fit looks extremely satisfying! The obtained parameters from the equation 1 are the following:

τ_H	τ_D	τ_{NZ}	c_{NZ}/c_1
5.8 s	246 s	5 s	0.13

It is interesting that predicted τ_{NZ} should be around 50 ms, and the estimated c_{NZ} is about a hundred times bigger than expected! This phenomenon may be explained by **hidden spins** that should be close to the electron and contribute to its heat capacity and extend its relaxation time

Experiments on the X-nuclei

It is common for DNP to polarize heteronuclei with further dissolution of the sample. The heat capacity of such nuclei is usually much smaller than of H and D. This allows one to fit X-nuclei de/repolarization experiment by knowing only the properties of the pure DNP juice. Here we demonstrate the fitting result for phosphorus for the same sample with addition of 1 M KH_2PO_4 salt.

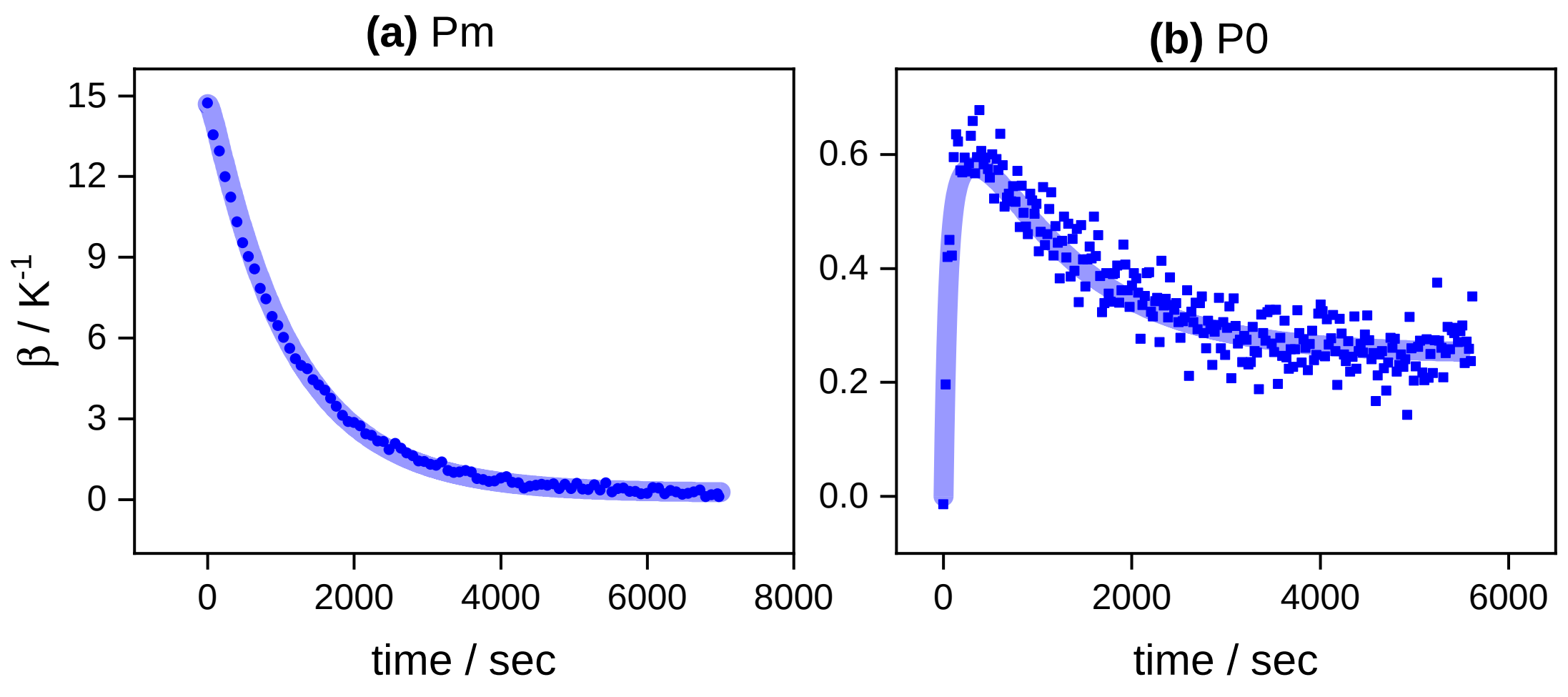

Figure 5: (a) de and (b) repolarization experiments for P

DNP juice || varying TEMPOL

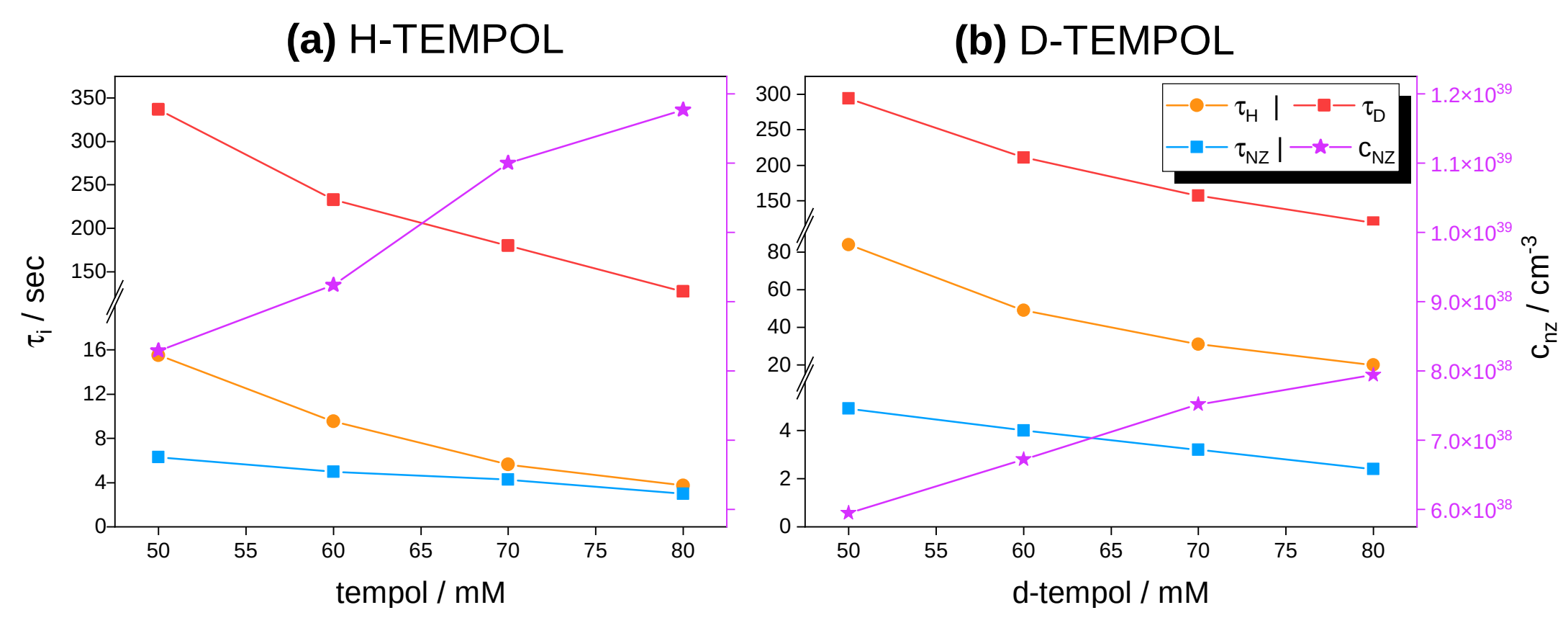

Figure 6: Parameters from 1 when the concentration of either (a) TEMPOL or (b) d-TEMPOL is varied

There are no too much surprises when the concentration of TEMPOL radical is varied. The characteristic interaction time for every nuclei become shorter which may be explained that electron-nuclei distances become shorter. Additionally, c_{NZ} become larger, cause the radical concentration is increased. Also, the c_{NZ} drops when changing H-TEMPOL to D-TEMPOL, which may indicate that H on TEMPOL contributes to c_{NZ}.

DNP juice || H/D ratio

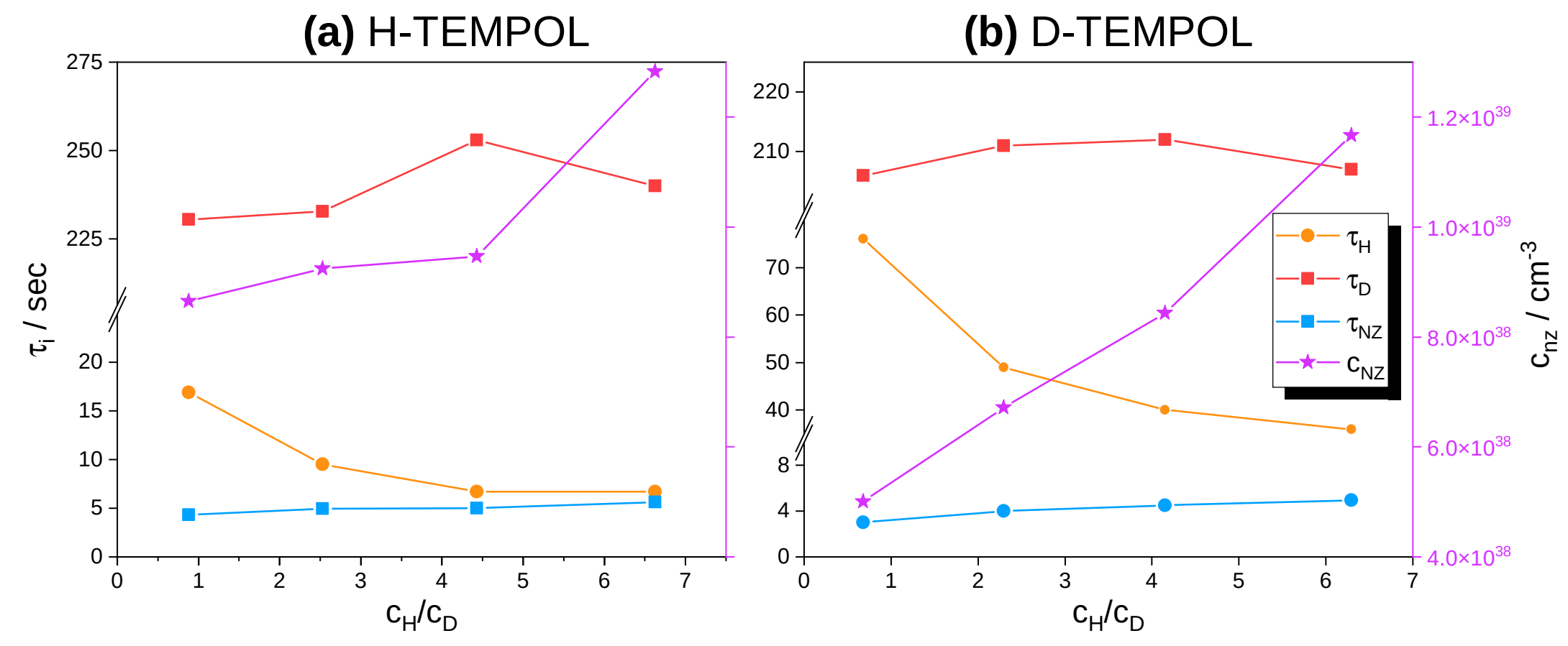

Figure 7: Parameters from 1 when H/D ration is varied for either (a)TEMPOL or (b)d-TEMPOL

When changing H/D composition, τ_H is decreased and τ_{NZ} is increased. The first can be explained by the reduction of the proton-electron distance. The second can be explained by increasing amount of the close protons prolonging fictitious relaxation time. Finally, the increasing c_{NZ} strongly indicated the existence of the hidden spin coming from the bulk protons.