Electronic Supplementary Material (ESI) for RSC Advances.

Quantitative description of the SABRE process: rigorous consideration of spin dynamics and chemical exchange

Stephan Knecht[a], Andrey N. Pravdivtsev[b,c], Jan-Bernd Hövener[a], Alexandra V. Yurkovskaya[b,c] and Konstantin L. Ivanov[b,c]

---

[a] University Medical Center Freiburg, 79098 Freiburg (Germany)
[b] International Tomography Center, Siberian Branch of the Russian Academy of Science, 630090 Novosibirsk (Russia)
[c] Novosibirsk State University, 630090 Novosibirsk (Russia)

Electronic Supporting Information

This ESI file contains (i) definition of the partial trace and direct product operators, (ii) relaxation super-operators and (iii) extended set of equations describing SABRE kinetics.

A. Derivation of Trace and Product Operators

In order to calculate the propagator of equation (5) from the main article we derived the Liouville space representations of the direct product and partial trace.

Let us consider two (square) density matrices $\hat{\sigma}^{(1)}$ and $\hat{\sigma}^{(2)}$, with Hilbert space indices i, j and m, n and dimensions denoted as $\dim\left(\hat{\sigma}^{(1)}\right)$ and $\dim\left(\hat{\sigma}^{(2)}\right)$, that are equal to the number of rows or columns in the corresponding matrices. The direct product of the two matrices is $\hat{\sigma}^P = \hat{\sigma}^1 \otimes \hat{\sigma}^2$. The elements of this direct product matrix $\hat{\sigma}^P_{kl} = \hat{\sigma}^P_{im,jn} = \hat{\sigma}^{(1)}_{ij} \cdot \hat{\sigma}^{(2)}_{mn}$ are obtained using the following index relation:

$$\begin{aligned} k &= (i-1) \cdot \dim(\hat{\sigma}^2) + m \\ l &= (j-1) \cdot \dim(\hat{\sigma}^2) + n \end{aligned} \tag{1}$$

The resulting dimensionality of $\hat{\sigma}^P$ is given by the product of dimensionalities:

$$\dim(\hat{\sigma}^P) = \dim(\hat{\sigma}^1) \cdot \dim(\hat{\sigma}^2) \tag{2}$$

Now let us demonstrate how one can go from the full density matrix $\hat{\sigma}^P$ to a partial density matrix, e.g., to $\hat{\sigma}^{(1)}$ by taking partial trance over subspace (2). The partial trace over the subspace that corresponds to operator $\hat{\sigma}^{(2)}$ results in the reduced matrix with elements:

$$\mathrm{Tr}_{(2)}\left(\hat{\sigma}_{kl}^{P}\right) = \sum_{m,n} \hat{\sigma}_{ij}^{(1)} \cdot \hat{\sigma}_{mn}^{(2)} \cdot \delta_{mn} = \sum_{m} \hat{\sigma}_{ij}^{(1)} \cdot \hat{\sigma}_{mm}^{(2)} = \hat{\sigma}_{ij}^{(1)} \cdot \mathrm{Tr}\left\{\hat{\sigma}^{(2)}\right\} \tag{3}$$

Thus, in this simplest example, the partial trace of the direct product is obviously equal to the matrix defined in the first subspace. Here δ_{mn} is the Kronecker delta. The same procedure is used in this work for performing the partial trace operation for general matrices (which are not necessarily given by the direct product of partial density matrices).

In this work, we also work in the Liouville space, where the density matrix is presented as a column vector. Thus, we need an index relation to transform a square matrix $\hat{\sigma}_{ij}$ from the Hilbert space into the Liouville space, where the resulting vector has only one index L, i.e., $\hat{\sigma}_L = \hat{\sigma}_{ij}$. The corresponding index relation is as follows:

$$L = (i - 1) \cdot \dim(\hat{\sigma}) + j \tag{4}$$

Thus, L changes from 1 to $\dim(\hat{\boldsymbol{\sigma}})^2$. Using these index relations the Liouville space representation of the direct product and partial trace are derived in a straightforward manner.

Partial trace. Each element $\{ij\}$ of the resulting reduced density matrix (in the first subspace), with the Liouville space index I, is calculated by summing up all elements with $m = n$ (in the second subspace), which belong to the same subspace $\{ij\}$, see equation (3). Essentially setting all elements of the trace operator that are included in the summation to 1. The second index, J, of the trace operator is a combination of equations (1) and (4) yielding the following trace operator:

$$\left\{\hat{\hat{S}}^{\mathrm{Tr}}\right\}_{IJ} = \delta_{mn} \tag{5}$$

The Liouville space indices, $\{IJ\}$, are:

$$\begin{gathered} I = (i - 1) \cdot \dim\left(\hat{\sigma}^{(1)}\right) + j \\ J = \left(\left((i-1) \cdot \dim(\hat{\sigma}^2) + m\right) - 1\right) \cdot \dim\left(\hat{\sigma}^{(1)}\right) \dim(\hat{\sigma}^2) + (j - 1) \cdot \dim(\hat{\sigma}^2) + n \end{gathered} \tag{6}$$

where $i, j \in \left\{1, \ldots, \dim\left(\hat{\sigma}^{(1)}\right)\right\}$, are the indices of the reduced dimensionality in the Hilbert space and $m, n \in \{1, \ldots, \dim(\hat{\sigma}^2)\}$ are the indices of the density matrix $\hat{\sigma}^2$ which is traced out.

Direct Product. The expression for the direct product operator is obtained in the same manner as the expression for $\hat{\sigma}_{kl}^{P} = \hat{\sigma}_{im,jn}^{P}$, i.e., by combining the index relations (1) and (4). The product of each element of $\hat{\sigma}_{mn}$ and $\hat{\sigma}_{ij}$ is calculated by selecting the correct element (of ij) using the index J (equation (8)) and then by placing the result at the correct position in the density matrix of the full space by using the index I (equation (8))

$$\left\{\hat{\hat{S}}^{\otimes}\right\}_{IJ} = \left(\hat{\sigma}_{\mathrm{H}_2}^{in}\right)_{mn} \tag{7}$$

The Liouville space indices are:

$$\begin{gathered} I = \left(\left(\left((i-1) \cdot \dim\left(\hat{\sigma}_{\mathrm{H}_2}^{in}\right) + m\right) - 1\right) \cdot \dim\left(\hat{\sigma}^{(1)}\right) \dim\left(\hat{\sigma}_{\mathrm{H}_2}^{in}\right) + (j-1) \cdot \dim\left(\hat{\sigma}_{\mathrm{H}_2}^{in}\right) + n \\ J = (i-1) \cdot \dim\left(\hat{\sigma}^{(1)}\right) + j \end{gathered} \tag{8}$$

Where $i, j \in \{1, \dots, \dim(\hat{\sigma}^{(1)})\}$ are the indices of the substrate density matrix in the Hilbert space and $m, n \in \{1, \dots, \dim(\hat{\sigma}^{in}_{\mathrm{H}_2})\}$ are the indices of the density matrix if H_2: $\hat{\sigma}^{in}_{\mathrm{H}_2} = f_{p\mathrm{H}_2}\hat{\sigma}_{p\mathrm{H}_2} + f_{o\mathrm{H}_2}\hat{\sigma}_{o\mathrm{H}_2}$.

One can readily see that the superoperator $\hat{\hat{S}}^{\mathrm{Tr}}$ and $\hat{\hat{S}}^{\otimes}$ are non-square matrices because of the different dimensionality of the spin-state spaces of the substrate and SABRE complex: the substrate has (at least) two spins ½ less.

B. Relaxation Operator

Random fluctuations of magnetic interactions, which gives rise to spin relaxation, are contained in the time-dependent part of the spin Hamiltonian $\hat{H}_F$.

$$\hat{H}_F(t) = -\gamma \sum_i \left(B_x(t)\hat{I}_{ix} + B_y(t)\hat{I}_{iy} + B_z(t)\hat{I}_{iz}\right) \tag{9}$$

To treat relaxation, we employ a formulation of the Redfield relaxation theory[1] based on random fluctuating fields, which was previously used in the study of relaxation field dependency[2].

We are considering only the simple case of extreme narrowing regime where $T_1 = T_2$. Furthermore, we assume that the field fluctuations are uncorrelated for different nuclei and for different spatial dimensions, x, y, z. Under these assumptions we get the following expression for the relaxation operator.

$$R_{ij,i'j'} = \frac{1}{2}\left(2J_{ii',jj'} - \delta_{jj'}\sum_k J_{ki',ki} - \delta_{ii'}\sum_k J_{kj,kj'}\right) \tag{10}$$

The correlation super-matrix J is expressed via $\hat{H}_F(t)$ by equation (11):

$$J_{ii',jj'} = \int_{-\infty}^{\infty} \overline{\langle i|H_F(t)|i'\rangle\langle j|H_F(t+\tau)|j'\rangle} d\tau \tag{11}$$

These elements are calculated in the eigen-basis of the static Hamiltonian, see equation (12), main article. For isotropic random fields equation (12) holds:

$$\int_{-\infty}^{\infty} \overline{B_x(t)B_x(t+\tau)} d\tau = \int_{-\infty}^{\infty} \overline{B_y(t)B_y(t+\tau)} d\tau = \int_{-\infty}^{\infty} \overline{B_z(t)B_z(t+\tau)} d\tau = \frac{1}{T_1} \tag{12}$$

Where the average is taken over t and over ensemble. When the field fluctuations uncorrelated for different nuclei and spatial dimensions (as assumed here), equation (11) can be simplified into equation (13):

$$J_{i,i',j,j'} = \sum_{l=1}^{N} \frac{1}{T_{1l}} \left[\langle i|\hat{I}_{lx}|i'\rangle\langle j|\hat{I}_{lx}|j'\rangle + \langle i|\hat{I}_{ly}|i'\rangle\langle j|\hat{I}_{ly}|j'\rangle + \langle i|\hat{I}_{lz}|i'\rangle\langle j|\hat{I}_{lz}|j'\rangle\right] \tag{13}$$

Where the sum is taken over all N nuclei and T_{1l} are the high field relaxation constants. Combining these equations the Relaxation operator is readily calculated. The last step is conversion of $\hat{\hat{R}}$ into the Zeeman Basis via equation (14). When the basis transformation is given by a matrix $\hat{V}$ for super-operators the transformation matrix will be

$$\hat{\hat{V}} = \hat{V} \otimes \hat{V} \tag{14}$$

C. Extended System

As mentioned in the main article a more general set of differential equations can be formulated, as shown in equation (15), in order to take account of polarization transfer to Ir-HH and time-dependent supply of *p*H_2. However, the resulting set of equations is not linear and therefore no simple propagator can be derived.

$$\begin{aligned}
\frac{d\sigma_S}{dt} &= \hat{\hat{L}}_S\sigma_S - k_a[C_1]\sigma_S + k_d \cdot \mathrm{Tr}_{\mathrm{H}_2}(\sigma_C) \\
\frac{d\sigma_C}{dt} &= \hat{\hat{L}}_C\sigma_C + k_a\{\sigma_s \otimes \sigma_{C_1}\} - k_d\sigma_C \\
\frac{d\sigma_{\mathrm{H}_2}}{dt} &= \hat{\hat{L}}_{\mathrm{H}_2}\sigma_{\mathrm{H}_2} + k_{ex}[\mathrm{H}_2\,]\sigma_{C_1} - k_{ex}[C_1]\sigma_{\mathrm{H}_2} - W_0\sigma_{\mathrm{H}_2} + W_0([p\mathrm{H}_2]\sigma_{p\mathrm{H}_2} + [o\mathrm{H}_2]\sigma_{o\mathrm{H}_2}) \\
\frac{d\sigma_{C_1}}{dt} &= \hat{\hat{L}}_{C_1}\sigma_{C_1} + k_d \cdot \mathrm{Tr}_S(\sigma_C) - k_a[S]\sigma_{C_1} - k_{ex}[\mathrm{H}_2]\sigma_{C_1} + k_{ex}[C_1]\sigma_{\mathrm{H}_2}
\end{aligned} \tag{15}$$

Here we introduce two additional equations to the system describing the state of H_2 in solution, σ_{H_2}, and the state of the intermediate complex, σ_{C_1}. In addition, two more rates are introduced, which describe the exchange of hydrogen in solution with the external source (W_0) and the exchange of hydrogen with the reaction intermediate (k_{ex}). When the just mentioned rate constants are large compared to the substrate exchange (i.e. $k_d[C] \ll k_{ex}[\mathrm{H}_2][C_1] \ll W_0[\mathrm{H}_2^*]$), equation (15) can be approximated by the set of equations used in the main text.

References

[1] A.G. Redfield, *The theory of relaxation processes*, in: J.S. Waugh (Ed.), Advances in Magnetic Resonance, vol. 1, Academic, New York, **1965**, pp. 1–32.

[2] K. Ivanov, A. Yurkovskaya and H.-M. Vieth, The Journal of Chemical Physics, **2008**, 129, 234513.