

ACCELERATING NMR SPECTROSCOPY WITH LOW RANK CONSTRAINT ON TIME DOMAIN SIGNAL

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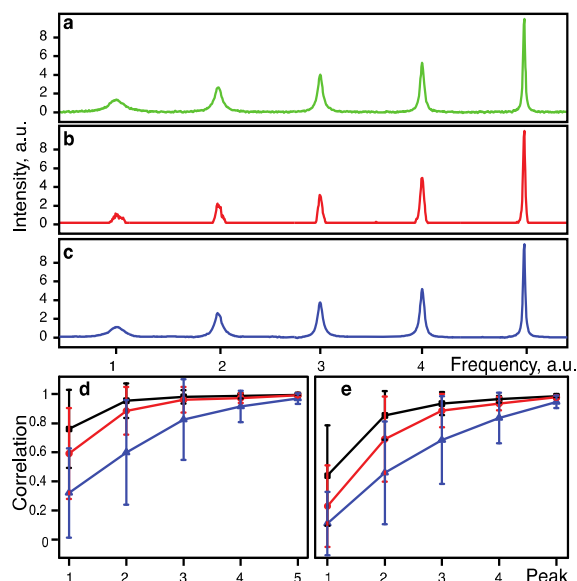


Figure 1. Reconstructions of the synthetic spectrum. (a) Fully sampled spectrum, (b) and (c) are the CS and LR reconstructions, respectively, obtained using 20% NUS. (d) and (e) are correlations between spectral intensities in small regions around the peaks in the full reference spectrum and the spectral reconstructions obtained using the LR and CS, respectively. The black, red, and blue lines in (d) and (e) correspond to the reconstructions using 20%, 15% and 10% NUS, respectively. The error bars are the standard deviations of the correlations over 100 NUS resampling trials.

according to a Poisson distribution¹³. The proposed LR method is compared with the state-of-the-art CS¹⁴. Figure 1 shows that the broadest peak to the left is faithfully recovered by the LR approach but is seriously distorted by the CS. For the three middle peaks with moderate line width, the CS produces clearly visible line shape distortions as shrinkage of the peaks. Correlation analysis indicate that the two broadest peaks are recovered systematically better using the LR than by the CS. Figure 2 shows the reconstructed spectrum of the intrinsically disordered cytosolic domain of human CD79b protein from the B-cell receptor. The CS is promising to reconstruct a spectrum assuming it is sparse. However, spectra with broad lines deviate from the sparseness assumption in CS thus line shape distortions and even suppression of signals might be observed.

Conclusion: A novel low rank reconstruction method to accelerate NMR spectroscopy is proposed. This new method produces faithful spectral reconstruction when the data are highly undersampled. It produces at least as good spectral reconstructions as the state-of-the-art compressed sensing (CS) and outperforms CS on recovering the broadest and weakest peaks, implying higher sensitivity of the LR method than CS. The new method is particularly useful for high throughput applications and studies of short lived systems.

Reference:

1. J. C. Hoch, M. W. Maciejewski, M. Mobli, et al., *Acc. Chem. Res.* **2014**, 47, 708-717.
2. Drori, I., *Eurasip J. Adv. Sig. Pr.* 2007, Article ID 20248.
3. Stern, A.S.; Donoho, D.L.; Hoch, J.C., *J. Magn. Reson.* 2007, 188, 295-300.
4. K. Kazimierczuk, V. Y. Orekhov, *Angew. Chem. Int. Ed.* 2011, 50, 5556-5559;
5. D. J. Holland, M. J. Bostock, L. F. Gladden, et al., *Angew. Chem. Int. Ed.* 2011, 50, 6548-6551;
6. Y. Shrot, L. Frydman, *J. Magn. Reson.* 2011, 209, 352-358;
7. X. B. Qu, D. Guo, X. Cao, S. H. Cai, Z. Chen, *Sensors* 2011, 11, 8888-8909;
8. S. G. Hyberts, A. G. Milbradt, A. B. Wagner, et al., *J. Biomol. NMR* 2012, 52, 315-327;
9. E. C. Lin, S. J. Opella, *J. Magn. Reson.* 2013, 237, 40-48.
10. P. Koehl, *Prog. Nucl. Magn. Reson. Spectrosc.* 1999;34:257-299.
11. H. M. Nguyen, X. Peng, M. N. Do, Z. P. Liang, *IEEE T. Biomed. Engin.*, 2013; 60:78-89.
12. J. F. Cai, E. J. Candès, Z. W. Shen, *SIAM J. Optimization* 2010; 20:1956-1982.
13. A. Ganesh, L. Zhouchen, J. Wright, W. Leqin, C. Minming, M. Yi, *CAMSAP'09*, 2009; pp. 213-216.
14. S. G. Hyberts, K. Takeuchi, G. Wagner, *J. Am. Chem. Soc.* 2010;132: 2145-2147.
15. M. Mayzel, K. Kazimierczuk, V. Y. Orekhov, *Chem Comm* 2014; 50: 8947-8950.

Abstract: Accelerating multi-dimensional NMR spectroscopy is important for chemical and biological study. Non-uniformly sampling (NUS) can dramatically reduce the data acquisition time and increase the sensitivity¹. A faithful reconstruction of a spectra from NUS data is impossible without introducing additional constraints. The sparse constraint has been applied in NMR spectroscopy, also called compressed sensing (CS)²⁻⁸.

In this work, we propose to reconstruct the spectra from NUS data with the low-rank (LR) constraint on the time domain signal. This property has never been exploited for NUS-NMR. The LR produces faithful spectral reconstruction when the data are highly undersampled. This new method outperforms the state-of-the-art CS method on recovering the broadest and weakest peaks, implying higher sensitivity is obtained using the LR method. The new method is particularly useful for high throughput applications and studies of short lived systems.

Method: The rank of the time domain NMR signal, called free induction decay (FID), is defined as the rank of a Hankel matrix^{9,10}. Let vector \mathbf{x} be the complete FID and the operator \mathbf{R} converts the FID into a Hankel matrix $\mathbf{X} = \mathbf{R}\mathbf{x}$. The LR of the FID means that the rank of its Hankel matrix \mathbf{X} is low. The spectrum reconstruction is solved by LR minimization problem:

$$\min_{\mathbf{x}} \|\mathbf{R}\mathbf{x}\|_* + \frac{\lambda}{2} \|\mathbf{y} - \mathbf{U}\mathbf{x}\|_2^2 \quad (1)$$

where \mathbf{y} is the acquired NUS FID data, \mathbf{U} is an operator of the NUS schedule, $\|\mathbf{R}\mathbf{x}\|_*$ is the nuclear norm¹¹ defined as a sum of matrix singular values, and λ trades the low rank constraint with the consistency between the reconstructed signal \mathbf{X} and the experimental data \mathbf{y} . The optimization problem is solved via alternating direction minimization method¹².

Result: One synthetic data and a 2D ¹H-¹⁵N HSQC spectrum are used in simulation. The NUS was performed

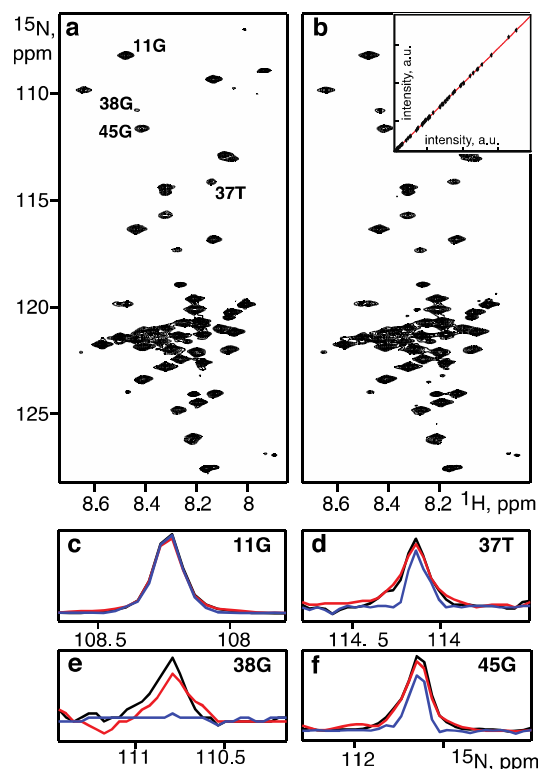


Figure 2. 2D ¹H-¹⁵N HSQC spectrum of the cytosolic domain of CD79b. (a) the LR reconstruction from 35% NUS data, (b) the fully sampled reference spectrum. The inset shows correlation of the peak intensities between the reference and the LR spectra; the correlation coefficient equals to 0.99. (c)-(f) representative reconstructions for the 11G, 37T, 38G, and 45G amide group peaks, respectively; black, red, and blue lines show 1D ¹⁵N-traces through the peaks in the full reference, the LR, and CS spectra, respectively.