POPULATION INVERSION AND COHERENCE EXCITATION IN NMR WITH AMPLITUDE MODULATED TEMPORALLY OVERLAPPED PULSES

by

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DEPARTMENT OF CHEMISTRY

Submitted
in fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI
INDIA

JUNE 2004

CERTIFICATE

This is to certify that the thesis entitled, **"POPULATION TRANSFER AND COHERENCE EXCITATION IN NMR WITH AMPLITUDE MODULATED TEMPORALLY OVERLAPPED PULSES"**, being submitted by Ms. Sonal Jain to Indian Institute of Technology, Delhi, for the award of Degree of Doctor of Philosophy, is a record of bonafide research work under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached requisite standard.

The works embodied in this has not been submitted, in part or fully to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

I take great pleasure in this opportunity to express my sincere gratitude and appreciation to the almighty and each and every person who has made the work for this thesis possible.

First and foremost I express my gratitude towards Dr. N. D. Kurur whose clear understanding of the subject and guidance in the right direction has made this work possible. His constant support and "try it out" attitude inspired me from the beginning till the end of my research. I am indebted to him for his counseling and various discussions that we had when I felt discouraged. His mature criticism towards my writing helped me in improving my writing skills.

I also extend my great thanks to Prof. B. Jayaram, Dr. A. Ramanan and Dr. Nalin Pant, for their valuable advice and help in the due course of the thesis. The discussions with Dr. V. K. Aggarwal and Prof. M. N. Gupta helped to build in me the confidence. I would like to thank them for this.

Many a thanks to all the faculty members and the departmental staff for their kind cooperation through the course of my work.

The credit also goes to Prof. Jaganathan from AIIMS, New Delhi, Prof. Anil Kumar from IISc, Bangalore and Prof. R. V. Hosur from TIFR, Mumbai for allowing me to use the spectrometer available and all the help without which none of the experiments would have been possible.

A lot of appreciation to all the past and present members of the lab, which include Rashmi, Harish, Ashutosh, Jaspreet and Ruchi with whom I have special relations. Special thanks to my friends Sampriya, Rajeev, Parul, Satish, Anil, Manpreet, Latha, Surojit, Pooja, Saher, Kumkum, Tarun, Pankaj for all the hilarious birthday treats and the nice time that I had spent with them.

This acknowledgement would be incomplete without the mention of Minakshi, Arunima and Mahesh. I would like to thank Minakshi for always being there by my side whatsoever the problem. I find myself privileged to be associated with her. I worked with Arunima in the lab during the work for my thesis, and share everything whether it is related to academics or not. Together we faced various situations, which will always remain in my memories. Mahesh helped me with the experimental aspect of NMR and I learned a lot in our short association.

I would like to express my sincere thanks on this occasion to my parents and my dear brother for taking all the pains and giving me immense support all the time when I was too busy to take care of myself. Their love, tolerance and sacrifice inspired me to come up to this stage in my life.

I owe a great deal to my in-laws for being a sturdy support all the time and their cooperation during the course of this work. Words are too little to appreciate their efforts.

Last but not the least I would like to acknowledge the support and patience of my husband Naresh for his cooperation and caring attitude, which motivated me to pursue my research in full enthusiasm during its last stages.

Financial assistance from DST and CSIR is gratefully acknowledged.

Sonal Jain

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ABSTRACT

There is a perennial search for shorter pulse sequences to achieve a particular transformation in NMR. In the present work, we extend Stimulated Raman Adiabatic Passage (STIRAP), a technique extensively studied in optics, to the NMR regime, demonstrate its capabilities for multiple quantum inversion & coherence excitation and discuss a couple of its applications in NMR. As the name suggests, the process describes a Raman type transition scheme with the characteristics of adiabatic passage. The concept is first developed to transfer the population in a three level system and is later extended for the population transfer and excitation in a multi-level system. In a three level system, population transfer is achieved by the application of two amplitude-modulated pulses, which are partially overlapped in time. To the best of our knowledge, the present work is the first attempt at extending STIRAP to the NMR regime and the first example of the use of partially overlapped pulses between connected transitions in the NMR regime.

STIRAP is described in a greater detail by considering a three level system- an initially populated level 1 and two unpopulated levels 2 and 3. It involves a Stokes pulse, Ω_s, driving the transition between the initially unpopulated levels 2 and 3, and a partially temporally overlapped pump pulse, Ω_p, connecting levels 1 and 2. Coherent interaction of the energy states leads to the eigenstates known as adiabatic states of the coupled system. One of the adiabatic states contains only components of the initial populated and final unpopulated level, as shown below:

$$|a_0\rangle = \cos\theta\,|1\rangle - \sin\theta\,|3\rangle$$

This state has no contribution from the intermediate level and is hence independent of its properties. During evolution, the system remains in this state i.e. if the system starts in $|1\rangle$ and as θ varies adiabatically from 0 at the beginning to $\pi/2$ at the end of the pulse, the population which was initially in $|1\rangle$ gets transferred to $|3\rangle$.

The implementation of the technique in NMR is complicated by the fact that in NMR unlike in the optical regime we are not dealing with pure states. Our computer simulation studies indicate its feasibility in NMR systems. We also provide experimental evidence. Earlier proposed extensions of STIRAP to achieve population transfer in multilevel systems are also described.

In NMR, the implementation of STIRAP in two and three-spin ½ scalar-coupled system are shown. In the two spin case, double and zero quantum population inversion i.e. $|\alpha\alpha\rangle \rightarrow |\beta\beta\rangle$ and $|\alpha\beta\rangle \rightarrow |\beta\alpha\rangle$ respectively are achieved. In STIRAP, two amplitude-modulated pulses that are temporally overlapped are applied to achieve inversion that otherwise would require the application of three sequential pulses between the connected transitions. Results from both simulation and experiments are shown. The experiments are performed on coumarin, which serve as an example for a two spin-half scalar-coupled AX system and on the three-spin AMX system in 2-3 dibromo propionic acid. For both the AX and AMX systems, inversion of population is achieved over a range of pulse lengths, which is of the order of hundred of milliseconds. Inversion is achieved irrespective of the exact shape of the amplitude-modulated pulses when the overlap between the two pulses ranges between 50-80% with the maximum at ~ 50%.

The utility of STIRAP in creating the coherent superposition of quantum states differing by more than one quantum is another focus of this thesis. There are a few STIRAP variants to excite the multiple quantum coherence and one such technique is fractional STIRAP or F-STIRAP. As described, on applying the pulses in the prescribed fashion the population evolves smoothly from state $|1\rangle$ to the coherent superposition $1/\sqrt{2}$ $(|1\rangle-|3\rangle)$ finally. If $|1\rangle$ and $|3\rangle$ correspond to $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$ then this state corresponds to double quantum coherence. Experimental results demonstrating the excitation of double quantum coherence in cytosine and coumarin are presented here. A detailed study on multiple quantum excitation efficiency suggests that the technique is reasonably robust to offset variations. The effect of pulse overlap on double quantum excitation is also presented.

Lastly, we investigated the application of these shaped pulses for two NMR applications: a) Decoupling of ^{2}H from ^{13}C and b) Enhancement of central transition in a quadrupolar nuclei

a) The decoupling of deuterium is usually achieved by the excitation of double quantum excitation. However, the inversion of deuterium if carried out fast enough, the spin ½ nucleus does not feel the effect of deuterium spins. In this chapter we show that STIRAP can be used for deuterium decoupling. The results from both the computer simulation and experiment (performed on $CDCl_3$) show the effective decoupling of deuterium. Computer simulations results show that the decoupling of deuterium is feasible over a range of rf field i.e. upto 15 kHz while the quadrupolar coupling constant is 30kHz.

b) The central transition is the only transition not affected by the quadrupolar interaction to first order in perturbation theory being only by it affected to second order. Hence, often in quadrupolar NMR nuclei only the central transition is excited. The population difference between the outermost levels in quadrupolar nuclei is maximum. Transferring the population from the outermost levels to the central levels can enhance the intensity of the signal obtained by the excitation of central transition. This transfer can be achieved by using the cascade of amplitude-modulated pulses described above. The simulations that were carried out on ^{23}Na and ^{17}O i.e. four and six level systems respectively, suggest that with modest rf power of 100-200 Hz, and the pulse lengths between 0.1-0.01 seconds, the central transition can be increased upto five times (for ^{17}O) over the equilibrium case. Initial experimental results obtained on ^{23}Na in an oriented medium are presented. The experimentally observed enhancement is lower than the theoretical expectation of $2I$.

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