NMR of Noncovalent Interactions: Utilizing NMR to Elucidate Protonation and Proton Transfer Mechanisms

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This presentation explores the use of NMR chemical shifts to study noncovalent interactions in both solution and solid-state environments. The investigation of these interactions through experimental NMR chemical shifts, combined with DFT calculations, highlights several key challenges.

The presentation examines examples of hydrogen bonds with experimentally confirmed geometries and dynamics, yet whose underlying mechanisms remain poorly understood.[1—5] The primary reason for this lies in our inability to accurately account for environmental effects in theoretical models. For most systems, well-defined requirements exist, including precise molecular geometry, the application of the Polarizable Continuum Model approximation, and the consideration of all direct noncovalent interactions involving the NMR-active nucleus or electronically conjugated fragments. However, these criteria are insufficient for molecular systems with highly polarizable electron densities, requiring the inclusion of an external electric field, whose exact magnitude must be determined independently.[6,7]

Secondly, the conversion of theoretically calculated NMR shieldings into experimental chemical shift scales necessitates knowledge of the absolute shielding of a reference molecule. This issue is discussed using examples from ^{31}P [8] and ^{15}N [9] NMR spectroscopy.

Finally, the presentation addresses the need for relativistic corrections in DFT calculations of NMR chemical shifts, particularly for coordination complexes involving heavy metals. While such corrections are unnecessary for elements in the first three rows of the periodic table—provided they are not covalently bonded to heavy elements—they become indispensable for elements from the fifth period onward. [10,11]

1. Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H.; *J. Am. Chem. Soc.* **2003**, *125*, 11710.
2. Lesnichin, S. B.; Tolstoy, P. M.; Limbach, H.-H.; Shenderovich, I. G.; *Phys. Chem. Chem. Phys.* **2010**, *12*, 10373.
3. Gurinov, A. A.; Lesnichin, S. B.; Limbach, H.-H.; Shenderovich, I. G.; *J. Phys. Chem. A* **2014**, *118*, 10804.
4. Ip, B. C. K.; Andreeva, D. V.; Buntkowsky, G.; Akcakayiran, D.; Findenegg, G. H.; Shenderovich I. G.; *Micropor. Mesopor. Mater.* **2010**, *134*, 22.
5. Shenderovich, I. G.; Denisov, G. S.; *Molecules* **2020**, *25*, 436.
6. Chernyshov, I.Yu.; Vener, M.V.; Shenderovich, I.G.; *J. Chem. Phys.* **2019**, *150*, 144706.
7. Shenderovich, I.G.; *J. Chem. Phys.* **2020***, 153,* 184501.
8. Shenderovich, I.G.; *Chemistry - Methods* **2021**, *1*, 61.
9. Shenderovich, I.G.; *J. Phys. Chem. A* **2023**, *127*, 5547.
10. Shenderovich, I.G.; *Molecules* **2021***, 26,* 1390.
11. Shenderovich, I.G.; *ChemPhysChem* **2024**, *25*, e202300986.