

## Correlated Vibrational Dynamics of DNA Base Pairs

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Hybrid QM/MM molecular dynamics simulations have been carried out for the Watson-Crick base pair of 9-ethyl-8-phenyladenine and 1-cyclohexyluracil in deuteriochloroform solution at room temperature [1]. Trajectories are analysed putting special attention to the geometric correlations of the N-H...N and N-H...O hydrogen bonds in the base pair. Even though the two hydrogen bonds are only approximately linear and the heterocycles are tilted with respect to each other, hydrogen bond and N-H lengths follow a simple empirical correlation based Pauling's valence bond order model.

In order to describe the IR line shape of the two NH stretching vibrations, the correlation between their fundamental transition frequencies and the hydrogen bond lengths is exploited. This facilitates efficient determination of the fluctuating transition frequencies along the QM/MM trajectory. Using IR line shape theory, the fundamental NH stretching transitions are obtained in reasonable agreement with experiment [2]. Analysis of the frequency correlation functions is shown to provide insight into anharmonic couplings to low-frequency modes that are responsible for the line broadening.

Finally, the line shape function is used to explore the dynamics of the two hydrogen bonds on the basis of the two-dimensional IR spectrum. The shape of the off-diagonal peaks in the spectrum reveals clear signatures of positive correlation between the two stretching vibrations.

[1] Y. Yan, G. M. Krishnan, O. Kühn, *Chem. Phys. Lett.*, **464** (2008) 230

[2] S. Woutersen, G. Cristalli, *J. Chem. Phys.*, **121** (2004) 5381