THz Fingerprinting of Biomolecules Supported by Ab Initio Molecular Modelling

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Abstract— In this paper we explore various *ab initio* molecular approaches and their usefulness for the prediction of vibrational spectra of biomolecules.

I. INTRODUCTION

Ab initio molecular orbital calculations and density functional theory have long been versatile tools in vibrational spectroscopy of biomolecules. In a previous study [1] we have investigated the use of *ab initio* molecular orbital calculations of frequencies in the far-infrared region for the identification of biomolecules. We now investigate the influence of different theoretical approaches[1] on the resulting vibrational frequencies. As an example we consider all-*trans*-retinal, a molecule fundamental in the transduction of light.

II. THEORETICAL APPROACH

There is a wide range of different levels of theory available for molecular modelling — the choice depending on the kind of system to be investigated. Hartee-Fock (HF) theory is a single-particle approximation, which is computationally accurate and relatively inexpensive. For our calculations of the vibrational frequencies we initially used the split valence basis set 6-31G for which additional functions are allocated to each valence atomic orbital. Subsequently, we implemented polarization basis sets 6-31G* and 6-31G** into our calculations. These basis sets allow for the possibility of non-linear displacement of charge away from the atomic centers. This is particularly important for systems containing small strained rings as in the case of retinal. As HF theory cannot adequately treat the correlation motion of electrons that occur due to electron-electron interactions, an overestimation of vibrational frequencies is a common systematic error. To overcome this, hybrid combinations of DFT and HF can be used, such as B3LYP (Becke's three-parameter hybrid [2] in combination with gradient-corrected correlation functionals by Lee, Yand and Parr [3]). The disadvantage of this theory is that it is computationally expensive. Gervasio *et al* [4] showed good agreement between experimental and calculated data using this approach and our initial DFT studies support this result.

[1] This is explored further in another paper in this proceedings, see Rainsford *et al.*

III. RESULTS

Comparison of our calculated results with experimental data [4] shows significant improvement in using the 6-31G** basis set rather than 6-31G or 6-31G*. To confirm these results we intend to do further experimental as well as theoretical studies on a number of related biomolecules. We would also like to investigate the influence of anharmonic vibrational corrections on the calculation of low frequency modes since our current studies only use scaling factors to correct the harmonic vibrations.
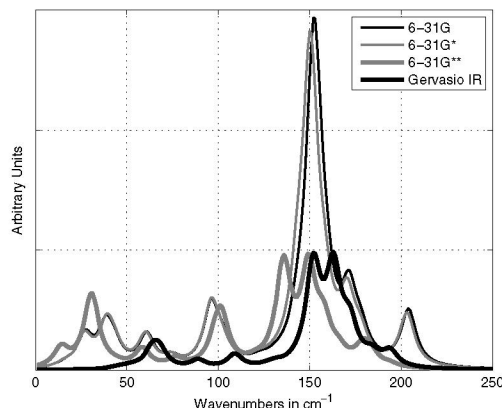

Fig. 1.   Calculated vibrational frequencies in the THz range using different basis sets and appropriate scaling factors [5] compared to far-infrared data [4]. The reference experimental data is included only in consideration of the frequency modes, not their absolute intensities as only relative values were provided by Gervasio *et al.*

REFERENCES

[1] I. Jones, T. Rainsford, B. Fischer, and D. Abbott, "Towards T-ray spectroscopy of retinal isomers: A review of methods and modelling", *Vibrational Spectroscopy*, 2006, in press.

[2] A. D. Becke, "Density functional exchange energy approximation with asymptotic behaviour", *Physical Review*, vol. A38 (6), pp. 3098-3100, 1998.

[3] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation energy formula into a functional of the electron density", *Physical Review*, vol. B37 (2), pp. 785-789, 1988.

[4] F. L. Gervasio, G. Cardini, P. R. Salvi, and V. Schettino, "Low-frequency vibrations of all-*trans*-retinal: far-infrared and raman spectra and density functional calculations", *J. Phys. Chem. A*, vol. 102, pp. 2131-2136, 1998.

[5] A. P. Scott and L. Radom, "Harmonic vibrational frequiencies: an evaluation of Hartree-Fock, Moller-Plesset, Quadratic confuguration interaction, density functional theory, and semiempirical scale factors", *J. Phys. Chem*, vol. 100, pp. 16502-16513, 1996.