Ab Initio Molecular Modelling of THz Spectra

T. J. Rainsford, I. Jones and D. Abbott
School of Electrical & Electronic Engineering, The University of Adelaide, SA 5005, Australia.
tamath@eleceng.adelaide.edu.au

Abstract- **Molecular modelling can be used to predict and confirm THz spectra, and to gain information that may be difficult or impossible to obtain experimentally. There are a variety of approaches, and consideration must be given to the likely sources of error in the molecular modelling of THz modes.**

I. AB INITIO MOLECULAR MODELLING

Molecular modelling techniques are useful for predicting spectra, assigning vibrational modes and obtaining information that is difficult or impossible to obtain experimentally. There is a wide range of molecular modelling and quantum chemistry techniques: *Ab Initio* techniques are the most accurate, do not depend on experimental input data and are broadly useful for studying systems composed of tens of atoms; however, they are computationally intensive. In these *Ab Initio* approaches the Schrödinger equation leads to direct quantitative predictions of chemical phenomena requiring as input only the masses and charges of electrons and nuclei. Few problems are tractable and so approximate mathematical models for which the solutions may exist need to be employed. Commonly, molecular orbitals, expressed as linear combinations of a finite set of one-electron basis functions, are used to approximate electron distributions and motions. Typical engines used for *Ab Initio* calculations are Gamess [1] and Gaussian [2], and have incorporated many standard basis sets although non-standard sets can be specified as required.

II. SOURCES OF ERROR

The greatest source of error is associated with the selection of equilibrium geometry - a slight change in bond length can lead to a considerable frequency shift. Errors may be inherent to inaccuracies of differentiation techniques required in the evaluation of the matrix force constants. Inclusion of higher-order effects such as vibrational anharmonicity and vibration-rotation interactions can improve fundamental frequencies by a few percent and are likely to be relevant to the low frequency modes of large biomolecules. Other error sources include approximations made in the actual approach: non-relativistic reduction, use of linear combinations of atomic orbitals, Born-Oppenheimer and single particle approximations. Post Hartree-Fock (PHF) methods such as configuration interaction, Moller-Plesset perturbation and density functional theory (DFT) are calculations that can be "added on" to take into account these errors. Considerable enhancement are achievable through improved basis sets which include additional functions that allow for atomic orbitals to adjust independently to a given molecular environment; polarization functions that describe the non-uniform displacement of charge away from atomic nuclei; or diffuse s- and p- type Gaussian functions. High angular momentum basis sets can account for higher-order interactions between electrons. When augmented with diffuse functions, they represent the most sophisticated basis sets available.

III. MODELLING IN THE LOW FREQUENCY REGIME

In general, the choice of basis set is a compromise. While it is desirable to achieve the highest level of accuracy this is not always required or, as in the case of large unsymmetrical biomolecules, computationally infeasible. Our initial results are interesting as they show that the basis sets used do have an important overall effect on the results. This is not unexpected. However, the actual method used does not provide a uniform improvement, Fig. 1. DFT leads to higher accuracy in the far infrared range but the frequencies in the very far infrared are not improved. It is possible that PHF methods do not significantly enhance accuracy in the THz regime. This will need to be tested with further calculations and other molecules.

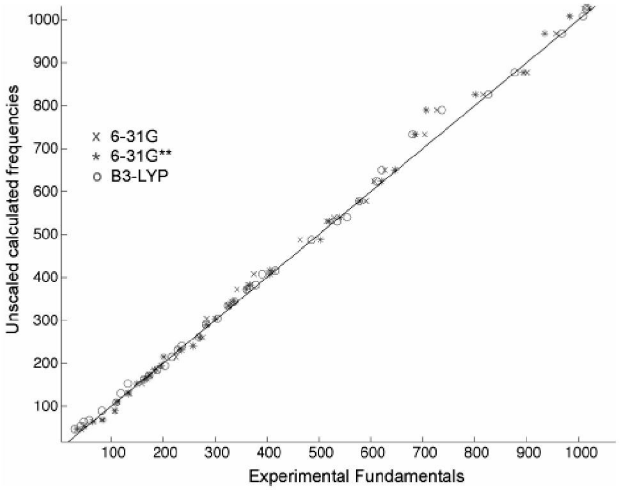

Figure 1. Three different calculated frequency sets compared with experiment. Experimental data in the range 40-400cm^{-1} is from Gervasio et al [3] and data from 400-1000cm^{-1} is our own FTIR data.

REFERENCES

[1] M.F. Guest, I.J. Bush, H.J.J. van Dam, P. Sherwood, J.M.H. Thomas, J.H. van Lenthe, R.W.A. Havenith, J. Kendrick, Molec. Phys. 103 (6-8) (2005) 719–747.

[2] M.J. Frisch, et al., Gaussian 94, Revision D.3, Gaussian Inc., Pittsburgh, PA, 1995.

[3] 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.