MODELLING THE STRUCTURE AND VIBRATIONAL SPECTRA OF SULPHONATE ANIONS: PROBLEMS TO KNOW AND OVERCOME.

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Abstract: *Ab initio* and DFT calculations have been performed on small alkyl-chain sulphonate anions, methanesulphonate (MS), ethanesulphonate (ES) and mercaptoethanesulphonate (MES). Results have been compared to experimental infrared and Raman spectra, and crystallographic structures. Problems are encountered when trying to accurately model the vibrational spectra of species containing hyper-valent sulphur, especially when using B3-LYP.

Given the abundance of sulphonated species in a wide range of pharmaceutical products, there appears to be a lack of high quality *ab initio* calculations to support and improve parameterisations found in common molecular modelling software. Indeed, whilst trying to accurately predict the vibrational spectra of our own self-assembled monolayers of MES, it soon became apparent that a great deal of care needs to be taken with this class of molecules, more so than most other "simple" systems. To this extent, it was necessary to return to the simplest example of an organic sulphonate anion: methanesulphonate.

The geometry of the anion was optimised using a wide range of basis sets employed in conjunction with HF, post-SCF MP2, and DFT levels of theory. Interestingly, even achieving a close correlation between the calculated geometry and the published crystal structure of NaMS[1] proved difficult. As with most anions, diffuse functions are required to obtain an accurate model. Hartree-Fock calculations afforded r(CS) values which were consistently too long, often by 0.07 Å. In fact, this picture becomes much worse using B3-LYP: the r(SO) and r(CS) bonds are overestimated using the B3-LYP functional, with the most accurate results being for the 6-31++G(3df,3pd) basis set (where r(CS) and r(SO) are overestimated by 0.056 Å and 0.010 Å, respectively). MP2 improves upon the results of B3-LYP: a shortening is observed for r(CS) and, to a lesser extent, r(SO) although predicted bond lengths remain elongated compared to experimental data. However, use of the recently described KM-LYP functional[2] affords accurate geometric parameters.

A further failing of B3-LYP is revealed when calculating the vibrational spectrum of the MS anion. Previous studies have treated methanesulphonic acid only at the HF level[3]. The strongest bands in the Raman spectrum, bands assigned to the ν(CS) and $\nu_s(SO_3)$, occur at *ca*. 790 and 1060 cm^{-1}, respectively[4]. Unscaled B3-LYP calculations give bands that are too low in value, even with the addition of diffuse functions to the heavy atoms, e.g. B3-LYP/6-311+G(d,p) predicts bands at 712 and 977 cm^{-1}. Addition of further polarisation functions to (using 6-311+G(3df,3pd)) yields the best fit to the experimental spectrum at the B3-LYP level, giving bands at 731 and 1034 cm^{-1}. Using MP2 theory slightly improves the fit of these two bands in comparison with the corresponding calculations at the B3-LYP level. MP2/6-311+G(d,p) was found to give the most satisfactory fit to the experimental data, within hardware restrictions. However, scaled KM-LYP/6-31+G(d,p) calculations gave an excellent fit to the experimental spectra at a fraction of the computational cost of the MP2 calculations.

A full conformational search produced four stable conformers for the MES anion at the HF, B3-LYP and MP2 levels. These structures correspond to, in order of decreasing stability, TG2g1, TTg2, TTt and TG2e2, where the nomenclature XYz signifies the conformation around the C-SO_3, C-C and C-SH bonds, respectively. The TG2g1 structure is stabilised by *ca.* 500 cm^{-1} upon inclusion of electron correlation. Unfortunately, no known crystal structure of NaMES has been published, hindering comparison to experimental data. Nevertheless, comparison with similar molecules indicates that bond lengths are overestimated with at both the B3-LYP and MP2 levels, similar to the case for the MS anion.

The vibrational spectrum depends, above all, on whether the C-C bond is in a *gauche* or *trans* configuration. Both the ν(CS) bands are shifted by *ca.* +40 cm^{-1} and their relative intensities are reversed upon the transition from *gauche* to *trans*. Even accounting for this fact, the actual fit to the experimental data remains unsatisfactory at the B3-LYP and MP2 levels. In cases, the $\nu_s(SO_3)$ band is predicted to be 120 cm^{-1} too low after scaling. This may arise partially from a truncated basis set required to accommodate the increased size of the MES anion compared to MS. However it is interesting to note that the KM-LYP method affords an accurate fit to both the Raman and infrared spectra, shown in Fig. 1.

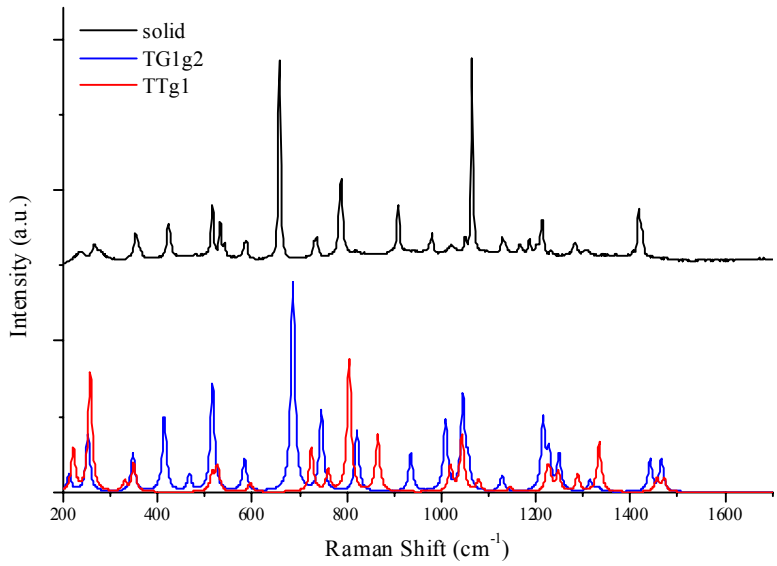

Fig. 1. Comparison of Raman spectrum of NaMES: (lower) calculated at the scaled KM-LYP/6-31+G(d,p) level; (upper) experimental.

From Fig. 1 it can be seen that the MES anion is present predominantly as the *gauche* conformer in the solid sample, although the medium intensity band at 787 cm^{-1}, and possibly the weaker band at 908 cm^{-1}, are evidence for presence of the *trans* conformer. Similar conclusions can be drawn upon comparison of the experimental and calculated infrared spectra. Upon solvation in water, the *trans* conformer becomes dominant although a medium intensity band at 664 cm^{-1} shows that some of the MES anion remains in the *gauche* form.

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