

# ROVIBRATIONAL CORRECTIONS TO THEORETICAL NMR PARAMETERS FROM VPT2 METHOD

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Theoretical calculations of NMR parameters (nuclear isotropic shieldings and indirect spin-spin coupling constants) are essential to support nowadays experimental works and predict spectral parameters of new chemical compounds. However, the accuracy of calculated parameters depends on the inclusion of correlation effect, method of calculation, size and flexibility of the basis set, intermolecular interactions, temperature, as well as on corrections due to molecular rovibrations. The temperature corrections are about an order of magnitude smaller than zero point rovibrational corrections (ZPVC) and are usually omitted.

The ZPV corrections are necessary to obtain highly accurate theoretical NMR parameters. On the other hand, the calculations of ZPVC are very expensive and challenging (or impossible to accomplish) for larger molecular systems. Thus, mainly density theory methods and smaller basis sets are used to evaluate ZPVC.

The VPT2 method (second order vibrational perturbation theory) has been implemented by Vincenzo Barone in G 03 and G 09 versions of popular Gaussian program. It was claimed as “a fully automated technique” in a “black box” manner.

The aim of our work is to compare NMR parameters of several model molecules calculated at equilibrium and rovibrationally averaged geometry with experimental and high level theoretical results from the literature and to estimate the accuracy of calculations. The results of calculations using B3LYP hybrid density functional with selected Pople and Jensen basis sets will be discussed.

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