

Vibrationally averaged dipole moments of methane and benzene deuterated isotopologues

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Synopsis We applied an methodology to calculate accurate dipole moments of the deuterated isotopologues of methane and benzene [1]. This approach was used previously to predict the isotopic effect on dipole moments in a variety of apolar and polar molecules [2,3] and combines two methods implemented in the Dalton code [4]. To compute the breaking symmetry effect we employed an adiabatic correction called Finite Nuclear Mass Correction (FNMC) [5]. In order to account the vibrational effect we used the zero point vibrational correction (ZPVC) method, which consider the anharmonic force field and deviation from linearity of the molecular property [6].

Small dipole moments which appear in apolar molecules under isotopic substitution (mainly deuteration), offer potential for high resolution spectroscopy since these molecules possess pure rotational spectra. The dominant effect on the dipole moments comes from the changes of the molecular vibrational modes due to the larger inertia of the heavier isotopes.

A smaller but still measurable contribution comes from the electronic symmetry breaking due to the different isotopic mass and thus cannot be analyzed theoretically under the usual clamped-nuclei Born-Oppenheimer (BO) approximation.

Here, *DFT – B3LYP* finite nuclear mass correction (FNMC) calculations of vibrationally averaged (ZPVC) isotopic dipole moments of methane and benzene, which compare well with experimental values, are reported. These molecules were chosen because of their importance in many basic and applied fields, particularly in astrochemistry and atmospheric chemical-physics.

For methane, in to the principal vibrational contribution to the molecular asymmetry, FNMC accounts for the surprisingly large Born-Oppenheimer error of about 34% to the dipole moments. This unexpected result is explained in terms of concurrent electronic and vibrational contributions.

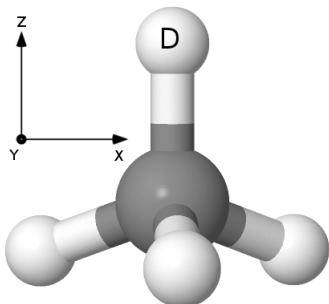


Figure 1. CH_3D isotopologue. The dipole moment lies in the z axis pointing $H \rightarrow D$.

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The calculated dipole moment of $C_6H_3D_3$ is about twice as large as the measured dipole moment of C_6H_5D . Computational progress is advanced concerning applications to larger systems and the choice of appropriate basis sets. The simpler procedure of performing ZPVC on the Born-Oppenheimer level and then adding the FNMC contribution at the equilibrium distance is shown to be appropriate.

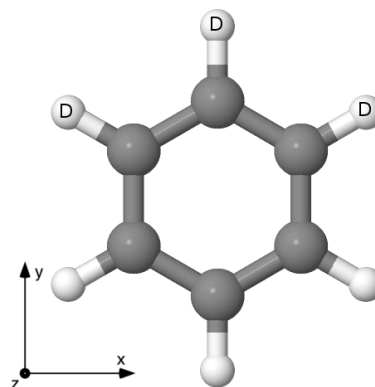


Figure 2. $C_6H_3D_3$ isotopologue. The dipole moment lies in the y axis pointing $H \rightarrow D$.

Also, the basis set choice is made by heuristic analysis of the physical behavior of the systems, instead of by comparison with experiments.

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