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Ab Initio Calculations of Torsionally Mediated Hyperfine Splittings in E States of Acetaldehyde

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Hyperfine splittings in methanol (CH_3OH) have been revisited in three recent publications.
[i] Coudert et al. [JCP 143 (2015) 044304] published an analysis of splittings observed in the low-J range. They calculated 32 spin-rotation, 32 spin-spin, and 16 spin-torsion hyperfine constants using the ACES2 package. Three of these constants (c_{zz}^0, $c_{zz}^{0,h}$ and $s_z^{0,h}$) were adjusted to fit hyperfine patterns for 12 transitions.
[ii] Three present authors and collaborators [JCP 145 (2016) 024307] analyzed medium to high-J experimental Lamb-dip measurements in methanol and presented a theoretical spin-rotation explanation that was based on torsionally mediated spin-rotation hyperfine operators. These contain, in addition to the usual nuclear spin and overall rotational operators, factors in the torsional angle α. Such operators have non-zero matrix elements between the two components of a torsion-rotation ^{tr}E state, but have zero matrix elements within a ^{tr}A state. More than 55 hyperfine splittings were successfully fitted using three parameters (c_{xx}^2, c_{yy}^2, and c_{xy}^2) and the fitted values agree well with ab initio values obtained in [i].
[iii] Lankhaar et al. [JCP 145 (2016) 244301] published a reanalysis of the data set from [i], using CFOUR recalculated hyperfine constants based on their rederivation of the relevant expressions. They explain why their choice of fixed and floated parameters leads to numerical values for all parameters that seem to be more physical than those in [i]. The results in (ii) raise the question of whether large torsionally-mediated spin-rotation splittings will occur in other methyl-rotor-containing molecules. This abstract presents ab initio calculations of torsionally mediated hyperfine splittings in the E states of acetaldehyde using the same three operators as in [ii], and spin-rotation constants computed by Gaussian09. We explore the first 13 K states for J from 10 to 40 and v_t = 0, 1, and 2. Our calculations indicate that hyperfine splittings in CH_3CHO are just below current measurement capability. This conclusion is confirmed by available experimental measurements.

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