AB INITIO RESULTS ON COUPLING BETWEEN THE LARGE AMPLITUDE TORSION AND SMALL AMPLITUDE VIBRATIONS IN METHANOL

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This talk will discuss *ab initio* structural and potential energy surface calculations carried out for methanol along the intrinsic reaction coordinate (corresponding to the large-amplitude torsion) from top to bottom of the torsional barrier. We will present our progress in interpreting the results in the context of coupling between the torsion and the small-amplitude vibrations. In the *ab initio* calculations, the first and second derivatives of the CH_3OH potential energy surface were obtained using MP2 perturbation theory in the Gaussian98 package. The changes due to the methyl group torsion were carefully examined in a detailed study of the angle dependence, with the IRC monitored about every 2.9^o at MP2/6-311+G(3df,2p) level using the VeryTight convergence criterion. Thanks to several new features in Gaussian98, all quantities under examination show smooth variation along the IRC path. Some preliminary results and conclusions are as follows: (1) The relation between the IRC and a torsional angle γ defined as the average of the three methyl dihedral angles was examined. As expected from the previous talk, the plot of γ against IRC contains a linear term plus a small but non-negligible *sine* contribution. (2) The symmetry behaviour with torsion was examined for both the optimized internal coordinates and the Hessian second derivatives. As we would expect, A' coordinates and $A'A'$ and $A''A''$ Hessian terms display a *cosine* variation with IRC while A'' coordinates and $A'A''$ Hessian terms display a *sine* variation. (3) Projected frequencies were determined along the IRC to explore the torsional variation of the 11 small-amplitude vibrational frequencies. The frequency shifts vary from 2 cm^{-1} for the most well behaved CO-stretch mode to 33 cm^{-1} for the OH-stretch mode, indicating that torsional coupling to the small-amplitude modes is very important in most cases. The results for the CH-stretching modes display an interesting resemblance to curves from a local mode picture. (4) From Fourier expansion of the optimized structures with respect to the IRC, coefficients of torsion-rotation parameters having (1-cos6γ) and sin3γ dependence can be obtained. This work is in progress.