ANALYSIS OF AB INITIO NORMAL-MODE DISPLACEMENT VECTORS ALONG THE INTERNAL ROTATION PATH FOR THE THREE C-H STRETCHING VIBRATIONS IN METHANOL

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Stemming from the observation of inverted A/E splittings for the ν_2 and ν_9 asymmetric CH-stretching modes in methanol, there has been much theoretical interest in attempting to explain the nature of the inversion. We have recently examined the ab initio normal-mode vibrational displacement vectors along the internal rotation path for the three C-H stretching vibrations in methanol, both in the symmetrized and non-symmetrized PAM coordinates. Graphical representations of the Cartesian atomic normal mode displacement vectors $d_i(\gamma)$ determined by the Gaussian suite of programs for the three CH stretching motions, $\nu_2(A_1), \nu_3(A_1)$ and $\nu_9(A_2)$, along the steepest-descent internal rotation path γ in methanol (CH_3OH) will be presented and discussed, where A_1 and A_2 are notations in permutation-inversion group G_6. These modes are interesting because the symmetry environment of each C-H bond changes significantly during the internal rotation, i.e., each of the methyl bonds takes turns passing (twice for a complete torsional revolution) through the plane of symmetry of the COH frame of the molecule. We present some simple theoretical models which can be used to help understand these displacement vectors. Although this is work in progress, some explanation is already possible for the rather irregular (avoided-crossing-like) behavior of these displacement vectors.