MULTIDIMENSIONAL TUNNELING IN 2-NITROTOLUENE[a]

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Although many non-rigid molecules displaying a single LAM have been spectroscopically characterized, less results are available about non-rigid molecules displaying several LAMs, as they are theoretically more challenging. This is confirmed by a recent spectroscopic investigation of nitrotoluene[b] which revealed that its 2-nitrotoluene isomeric species displays two LAMs corresponding to internal rotations of the CH_3 and NO_2 groups. In this investigation,[b] because no approach accounting for two LAMs was available, the microwave spectrum of 2-nitrotoluene was analyzed using a simplified approach accounting only for the torsional motion of the CH_3 group.

In this talk, the IAM water dimer formalism[c] will be applied to 2-nitrotoluene. As this theoretical approach is designed for multidimensional tunneling in the high-barrier limit, it is well suited for this species. Once the equilibrium configurations and the tunneling paths are chosen, the IAM approach[c] allows us to derive a fitting Hamiltonian accounting for the rotational dependence of the tunneling splittings, but not for their magnitude, which should be obtained fitting the spectroscopic data. In 2-nitrotoluene, there are six C_1 symmetry equilibrium configurations and two tunneling paths. The first and most feasible one corresponds to a $2\pi/3$ rotation of the methyl group. The second one is the complicated geared internal rotation of both the CH_3 and NO_2 groups identified using quantum chemistry calculations.[b]

The results of the line position analysis of the available microwave data[b] with the new IAM approach will be presented. It is hoped that the analysis results will be more satisfactory than with the simplified approach[b] and this will provide us with a better understanding of the 2-nitrotoluene multidimensional potential energy surface.

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[b]Roucou, Goubet, Kleiner, Bteich and Cuisset, *ChemPhysChem* **21** (2020) 1

[c]Hougen, *J. Mol. Spec.* **114** (1985) 395; and Coudert and Hougen, *J. Mol. Spec.* **130** (1988) 86