THE $g'Ga$ CONFORMER OF ETHYLENE GLYCOL: A TEST CASE FOR TUNNELING-ROTATION APPROACHES DEVELOPED FOR NON-RIGID MOLECULES

D. CHRISTEN, *Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, D-72076 Tübingen, Germany*; H. S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany*; AND L. H. COUDERT, *Laboratoire de Photophysique Moléculaire, C.N.R.S., Bât. 350, Université Paris-Sud, 91405 Orsay Cedex, France*.

Ethylene glycol $(CH_2OH)_2$ is a molecule of great interest because it displays intramolecular hydrogen bonding as well as an interconversion large amplitude motion which allows each OH groups to be put in turn into the hydrogen bond. This molecule also occurs in several conformers and at the present time only the two lowest lying forms have been spectroscopically characterized, namely, when listed with increasing energy, the $g'Ga^a$ and the $g'Gg^b$ conformers. As shown by the previous investigation,[a] in the $g'Ga$ conformer, the large amplitude motion leads to a large tunneling splitting of about 6.9 GHz which is Coriolis coupled to the overal rotation of the molecule. The new measurements of the millimeterwave spectrum carried out in Köln confirm these results. However, they involve transitions characterized by much higher J and K_a-values than those initially measured and the theoretical approach developed previously[a] did not allow us at first to account correctly for the observed frequencies.

The new data were first analyzed using an RAS fit program based on Pickett's formalism[c] and afterwards using a modified version of the IAM-like approach initially developed.[a] Although both theoretical approaches are designed to account for the Coriolis coupling between the large amplitude motion and the overall rotation of the molecule, they involve very different coupling terms. In the paper, the results of the two analysis will be presented. The differences and the analogies between the two theoretical approaches will be discussed and it will be stressed, using the results of both analyses, that there exists a transformation which allows us to obtain the spectroscopic parameters of the RAS fit[c] from those obtained in the IAM-like formalism,[a] and vice versa.

[a] Christen, Coudert, Suenram, and Lovas, *J. Mol. Spectrosc.* **172,** 57 (1995).
[b] Christen, Coudert, Larsson, and Cremer, *J. Mol. Spectrosc.* **205,** 185 (2001).
[c] Pickett, *J. Chem. Phys.* **56,** 1715 (1972).