THE DIRECT OBSERVATION AND ANALYSIS OF PSEUDOROTATION IN 1,3-DIOXOLANE

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A number of transitions identified as belonging to the rotational structure of $n = 0 \rightarrow n = 1$, $n = 2 \rightarrow n = 3$, and $n = 0 \rightarrow n = 3$ pseudorotational (PR) bands in 1,3-dioxolane were observed in the direct absorption experiment in the range of 153-364 GHz using the pulsed jet FASSST spectrometer.[a] The newly observed transitions have been analyzed together with the data available from microwave measurements.[b] The data were globally fit to a Hamiltonian similar to that which has been used in the analysis of tetrahydrofuran,[c] and the molecular constants of 1,3-dioxolane in the $n = 0...3$ pseudorotational states were determined. The frequencies of the newly observed PR bands, $n = 2 \rightarrow n = 3$ and $n = 0 \rightarrow n = 3$, along with the results of the microwave[b] and the low resolution FIR studies[d] were used in a global analysis to derive the potential barrier to pseudorotation in the molecule. $Ab\ initio$ calculations were also used to describe the potential surface along the pseudorotational path. The results of the modeling and comparisons between $ab\ initio$ and empirical surfaces will be discussed.

[a] D.Melnik, S.Gopalakrishnan, T.A.Miller, S.P.Belov and F.C.De Lucia, *J.Chem.Phys.*, **114**, 6100 (2001)
[b] P.A.Baron and D.O.Harris, *J.Mol.Spec.*, **49**, 70 (1974)
[c] D.Melnik, S.Gopalakrishnan, T.A.Miller and F.C.De Lucia, *J.Chem.Phys.*, **118**, 3589 (2003)
[d] J.A.Greenhouse and H.L.Strauss, *J.Chem.Phys.*, **50**, 124 (1969)