MICROWAVE SPECTRA OF MOLECULES WITH MULTIPLE CONFORMATIONS: 2,2,4-TRIMETHYLPENTANE

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The number of possible conformations in an organic molecule grows multiplicatively with the size of the C-C backbone. As the molecule of interest increases in chain length, it becomes more challenging experimentally and theoretically to determine the most favorable conformation. Moreover, as the number of possible conformations increases, the energy difference between the various conformers is expected to decrease, making it difficult to establish the ground-state conformer of the system. In the present work, we explore the problems of studying molecules which display a large number of potential conformations by examining the microwave spectrum of 2,2,4-trimethylpentane, the major component of gasoline. Semiempirical (AM1) and ab initio (HF/6-31G*) calculations are also undertaken on this system to help guide the experimental measurements and to explore the reliability of the theoretical methods for this relatively large molecule. Ignoring methyl-group rotations, the possible conformers differ by rotation about the C(2)-C(3) and C(3)-C(4) bonds. The theoretical calculations have identified three local conformational minima (A-C). The calculated relative energies for A, B, and C are 0, 250, and 1369 cm^{-1}, respectively, at the HF/6-31G* level. The barrier between the A and B conformers is calculated to be only 35 cm^{-1}. The molecular-beam Fourier-transform microwave spectrum of 2,2,4-trimethylpentane reveals a plethora of lines. At present, one set of a-type transitions have been assigned to one conformer of the molecule. The a-type transitions are split into doublets, separated by $\sim$ 5 to 50 MHz, suggestive of a splitting due to tunneling. Efforts are presently underway to complete the assignment of the spectrum.