# THE MOLECULAR STRUCTURE OF TETRACARBONYLDIHYDRORUTHENIUM - MICROWAVE MEASUREMENTS AND DFT CALCULATIONS

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The microwave rotational spectra for seven isotopomers of tetracarbonyldihydroruthenium were measured in the 4-12 GHz range using a Flygare-Balle type microwave spectrometer. The measured transition frequencies could be fit to within a few kHz using a rigid rotor Hamiltonian with centrifugal distortion. The rotational constants for the most abundant isotopomer are A=1234.2762(4), B=932.7016(6) and C=811.6849(6) MHz. The measured 21 rotational constants were used to determine the following structural parameters: r(Ru-H) = 1.710(23)$\AA$, r(Ru-C1) = 1.952(21) $\AA$, r(Ru-C3) = 1.974(28) $\AA$, $\angle$(H-Ru-H) = $87.4(2.4)^\circ$, $\angle$(C1-Ru-C2) = 160.6(4.3)°, $\angle$(C3-Ru-C4) = $101.4(1.5)^\circ$, and $\angle$(Ru-C1-O1) = $172.6(7.6)^\circ$. These structural parameters are in excellent agreement with the substitution coordinates determined from the Kraitchman equations, and with the structural parameters calculated using density functional theory. There was no previous structural data on this complex. The results of the microwave data and with theoretical calculations both indicate $C_{2v}$ molecular symmetry, and show that the H atoms are separated by about 2.36$\AA$. These results indicate that this complex is clearly a 'classical dihydride' rather than an $\eta^2$ - bonded, 'dihydrogen' complex. Fairly large deuterium isotope effects were observed for the Ru-H bond length and H-Ru-H angle. The $r_0$, Ru-D bond lengths were observed to be 0.033$\AA$ shorter than the $r_0$, Ru-H bond lengths. The D-Ru-D angle is $1.1^\circ$ less than the H-Ru-H angle indicating that the anharmonicity effects are larger for the bond lengths than for the interbond angle. The new results on this complex are compared with previous results on the similar dihydride complexes, $H_2Fe(CO)_4$, and $H_2Os(CO)_4$.