THE MOLECULAR AND ELECTRONIC STRUCTURE OF THE BROMINE DIOXIDE, OBrO, FREE RADICAL

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The OBrO radical has been observed in the gas phase above the solid products of the Br_2-O_3 reaction. The rotational spectrum has been studied for the first time in selected regions between 88 and 627 GHz in the (000), (01 0), and **(020)** states for both ^{79}Br and ^{81}Br isotopomers. The spectrum is that of an asymmetric top (κ = **-0.824)** with C_{2v} symmetry in the $^2B_1$ electronic ground state. The J and K_a quantum numbers cover the range 161 and 10-14 respectively. Rotational, centrifugal distortion, electron and nuclear spin-rotation, spin-spin, and nuclear quadrupole coupling constants have been determined, as well as centrifugal distortion terms for the c's and some of the hyperfine constants. The fine and hyperfine splittings as well as the related constants are substantially larger than those in the related OClO. The ratios between OBrO and OClO fine and hyperfine constants are consistent with ratios for the Br and Cl atoms. The molecular structure and the harmonic force field have been derived and are compared with data for related molecules.