

THE LABORATORY DETECTION AND GEOMETRICAL STRUCTURE OF THIOZONE (S<sub>3</sub>) AND TETRASULFUR (S<sub>4</sub>)

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Small sulfur clusters (S<sub>2</sub> – S<sub>8</sub>) are of significant fundamental and applied interest, but surprisingly little is known about the electronic ground state and structures from S<sub>3</sub> to S<sub>5</sub>. The rotational spectra of two, thiozone, S<sub>3</sub>, and tetrasulfur, S<sub>4</sub>, have now been observed for the first time by Fourier transform microwave spectroscopy. From the rotational constants of the normal and <sup>34</sup>S isotopic species, precise geometrical structures have been derived for both clusters with C<sub>2v</sub> symmetry. The derived structural parameters indicate substantial double bonding in S<sub>3</sub> and sp<sup>2</sup> hybridization of the apex sulfur atom; S<sub>4</sub> also has double bonding between the outermost S atoms, but the central bond is relatively long and weak, like that observed for S<sub>2</sub>O<sub>2</sub>.