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A Microwave Spectrograph with Backward-Wave Oscillators as Radiation Sources. Microwave Spectrum, Structure and hindered internal Rotation of Dimethyl Sulfide

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We have successfully operated a 30 kc-square-wave Stark-modulation microwave spectrograph employing backward-wave oscillators (« carcinotrons », CSF, Paris) as radiation sources and completely covering the frequency range from 8 to 37,5 kmc/s with 4 such tubes. The b.w.o.'s are IF-stabilized against the harmonics of a quartz-controlled yet continuously variable frequency standard (600-1000 mc/s), resulting in a source noise as low as with the best klystron sources. Tuning is effected by variation of the standard frequency. We believe that its wide-range single-control tuning makes the b.w.o. an ideal microwave source for spectroscopical work.

With this spectrograph we have studied the spectrum of $(CH_2)_2\,S$, an asymmetric rotor with two groups showing hindered internal rotation. Of the many spectral lines observed 29 could be assigned to their transitions. The structural analysis was based on the low-J transitions up to $J = 2$, all of which were found. Thus centrifugal distortion could be neglected. With the rigid rotor approximation and assuming C_3-symmetry of the methyl groups and the tetrahedron angle for $_{H}\diagup C \diagdown_{H}$, we determined the C—S and C—H bond lengths and the $_{C}\diagup S \diagdown_{C}$ angle. From the internal rotation splitting of certain low-J transitions we found the V_3-potential of the rotation hindrance to be 2090 cal/mole, following a theory developed by Swalen and Costain.
