THE ROTATIONAL SPECTRUM OF ACETONE IN THE SECOND EXCITED TORSIONAL STATE

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The second excited torsional state of acetone has been assigned in a room temperature rotational spectrum between 118 and 376 GHz recorded by the Fast Scan Submillimeter-wave Spectroscopic Technique (FASSST). At this point, over 500 rotational transitions from all four torsional substates AA, EE, AE and EA have been assigned by using the integrated programs CAAARS [a] (Computer Aided Assignment of Asymmetric Rotor Spectra) and ERHAM [b] (Effective Rotational Hamiltonian). The Loomis-Wood diagrams generated by CAAARS have been essential in identifying series of lines that belong neither to the ground state nor to the first excited torsional state of acetone. The assigned transitions were fitted with ERHAM to an effective rotational Hamiltonian for molecules with two periodic large-amplitude motions. The rms deviation of a fit of 483 frequencies to 32 parameters was 372 kHz. In the ground [c] and first excited torsional [d] states, the rms deviations for sub-mm wave frequencies with the same weight were 133 and 233 kHz, respectively. There are two possible reasons for the lower quality of the fit: 1) Most assigned transitions are rotationally degenerate with low K_a, making it difficult to determine precise spectroscopic parameters. 2) The splittings due to internal rotation are much larger than anything seen previously for similar molecules. For comparison, the torsional components of one transition are spread out over 102 MHz in the ground state, but over 2024 MHz in the second excited torsional state. Since this state is only about 50 cm^{-1} below the barrier to internal rotation, the method used by ERHAM may no longer be appropriate.

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