EXPERIMENTAL LINE PARAMETERS OF HIGH-J TRANSITIONS IN THE O_2 A-BAND USING FREQUENCY-STABILIZED CAVITY RING-DOWN SPECTROSCOPY

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The reliability of high-*J* line parameters in spectroscopic databases can affect the uncertainty budget of experiments aiming to utilize optical probing to study highly rotationally excited molecules. Ultra-cold collision dynamics of $O_2(E_{rot})$, specifically, has recently been suggested as an intriguing but experimentally demanding system. One possibility would be to directly probe absorption transitions of O_2 as it trickles down a ladder of rotational states via collisional relaxation following rotational excitation. In certain cases, another strategy might be to utilize optical absorption to probe the collision partner for O_2. Both of these experimental approaches require an understanding of the spectroscopy of elevated rotational states, and in particular the intensities and widths are important for quantifying molecular dynamics. In the case of rotationally excited species, these data would have to be obtained by extrapolation of line parameters from existing databases. Subtle deviations from the database line parameters, as revealed by experiments, may be amplified depending on how far in *J* the data are extrapolated. Our goals in this study are (I) to provide the highest-*J* spectroscopic measurements of line intensities and widths for the primary isotope of O_2 in the *A*-band region and (II) to understand how the line parameters compare to, and build on, what is contained in the widely used HITRAN database. The experiments presented here are challenging because these lines are some of the weakest ever observed in the laboratory, thus requiring extremely sensitive optical detection methods. We have measured transitions between *J*' = 32 and 50 (self-broadened) and *J*' = 32 and 42 (air-broadened) and have demonstrated a minimum detectable line intensity of $\sim 2\times 10^{-31}$ cm molec.$^{-1}$. Our highest *J* measurements probe lower states having rotational energies of $\sim$3775 cm^{-1}, 40% higher than the most extensive measurements to date.