OBSERVATION AND ANALYSIS OF THE $2\nu_3$ BAND OF $^{32}S^{16}O_3$

THOMAS A. BLAKE, ROBERT L. SAMS, *Pacific Northwest National Laboratory, P. O. Box 999, Mail Stop K8-88, 3020 Q Avenue, Richland, WA 99352 (PNNL is operated for the US Department of Energy by the Battelle Memorial Institute under contract DE-AC06-76RLO 1830)*; ARTHUR MAKI, *15012 24th Ave. S. E. Mill Creek, WA 98012*; TONY MASIELLO, JEFFREY BARBER, NICOLAE VULPANOVICI, ENGELENE t.H. CHRYSOSTOM, JOSEPH W. NIBLER, *Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331-4003*; ALFONS WEBER, *National Science Foundation, 4201 Wilson Boulevard, Arlington, VA 22230.*

We are engaged in a comprehensive investigation of the fundamental and low lying combination and overtone bands of the parent $^{32}S^{16}O_3$ as well as the $^{34}S^{16}O_3$, $^{32}S^{18}O_3$, and $^{34}S^{18}O_3$ isotopic variants of sulfur trioxide. CARS spectroscopy of the ν_1 Raman active bands has been performed at Oregon State University and high resolution infrared absorption spectroscopy of room temperature static cell samples has been performed at PNNL using a Bruker IFS 120 HR Fourier transform spectrometer. Results for the absorption spectrum of the $2\nu_3$ band of $^{32}S^{16}O_3$, recorded at a resolution of $0.0025\ \mathrm{cm}^{-1}$, will be presented. The overtone of the ν_3 fundamental $[(e')^2 = A_1' + E']$ is centered at $2777.87139(5)\ \mathrm{cm}^{-1}$with $B' = 0.3462802(2)\ \mathrm{cm}^{-1}$and $B'' = 0.34854336(4)\ \mathrm{cm}^{-1}$. Assignment and fitting of the perpendicular band shows that there is an internal perturbation that arises from a $\Delta k = \pm 2$, $\Delta l = \pm 2$ coupling of the $l = 0$ and $l = \pm 2$ components. A level crossing is evident with the $l = 2$, $k = 11$ levels pushed to higher energy and the $l = 2$, $k = 14$ levels pushed to lower energy, for example. We have determined that the band center of the perturbing dark state is approximately 11 cm^{-1}below that of the bright state. The Hamiltonian including perturbing terms and fit constants will be presented. In addition, ν_2, ν_3, and ν_4 have been measured and analyzed to reveal new details such as the splitting of the $K = 2$ and $K = 3$ levels.