ELECTRON-SPIN AND TUNNELING EFFECTS IN THE MICROWAVE SPECTRUM OF SO_2–O_2

A.R. HIGHT WALKER, G.T. FRASER, J.T. HOUGEN, C. LUGEZ, R.D. SUENRAM, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; W. FAWZY, *University of United Arab Emirates, Faculty of Science, P.O. Box 17551, Al-Ain, United Arab Emirates*.

The rotational spectrum of the SO_2–O_2 complex has been recorded between 6 GHz and 24 GHz using a pulsed-molecular-beam Fourier-transform microwave spectrometer. The spectrum is complicated by the spin of the triplet oxygen and tunneling of the two monomers within the complex. Approximately sixty *a*- and *c*-type transitions with J = 0 to 8 and K_a = 0,1,2. have been assigned and confirmed by combination differences. The observed transitions correlate to the lower ($\Omega = 0$) energy component of the O_2 spin-spin multiplet. Transitions associated with the higher energy ($\Omega = \pm 1$) component have not been assigned, presumably due to the lower population of this state in the cold molecular beam ($T_r = \sim 1$ K). We note that in free O_2 the spin-spin splitting is approximately 4 cm^{-1} (6 K). The ratio of the frequencies of the two observed $\Delta K = 1$ subband origins is approximately 1.6, compared to a value of 3 expected for a rigid prolate top. A tunneling motion which reverses the sign of the *c*-type dipole moment component is used to explain this anomaly. Such a tunneling motion is anticipated from previous studies on Ar-SO_2 and SO_2 dimer. A fit of the observed transitions to a rigid rotor Hamiltonian with a tunneling term produces a standard deviation of 23 MHz and a tunneling splitting of 2.3 GHz. This standard deviation is significantly greater than the experimental precision of ~1 kHz and is mainly attributed to the neglect of the electron spin. An alternative fit of this same data was carried out using a Hamiltonian which takes into account effects of electron spin and approximates a tunneling coefficient. This second fit produced errors on the order of 1 MHz and confirms that both the electron spin and the tunneling motion must be simultaneously considered. Future efforts are directed at developing a rotation-tunneling-spin Hamiltonian to model the spectrum. In addition, isotopic studies are being undertaken to determine the orientation of the SO_2 and O_2 subunits in the complex.