1 BrO AND 11 OBr: NEW RESULTS FOR FAMILIAR MOLECULES

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As part of a program at our laboratory to extend the spectroscopic data base of the halogen oxides and oxo-acids which participate in atmospheric ozone chemistry, we have continued the investigations on BrO and HOBr. The rotational spectra of the $^2\Pi_{1/2}$ $v = 0$ and 1 states as well as the $^2\Pi_{3/2}$ $v = 2$ state of normal BrO and the $^2\Pi_{3/2}$ $v = 0$ and 1 and $^2\Pi_{1/2}$ $v = 0$ states of $Br^{18}O$ have been observed for the first time. Observations of the $^2\Pi_{3/2}$ $v = 0$ and 1 states have been extended. Analysis of these new data along with previously published spectra has resulted in improvements in the precision of previously determined parameters as well as the first determination of others. In particular, the effects of isotopic substitution have been used to determine the electron spin-rotation coupling constant as well as the deviation of the rotational constant from the Born-Oppenheimer approximation.

The ν_1 and ν_2 bands of DOBr centered near 2673.2 and 853.4 cm^{-1} respectively and the millimeter spectra arising from its $v_2 = 1$ and $v_3 = 1$ states have been observed. The ν_1 band is perturbed by an anharmonic resonance ($\Delta K_a = 0$) with $3\nu_3 \sim \nu_2$. All rotational and vibrational spectra from both bromine isotopic species have been fitted with a single calculation. The perturbation in the ν_1 band has been well described. Equilibrium rotational and centrifugal distortion constants have been determined. The equilibrium structure which has been derived from the DOBr and HOBr rotational constants agrees well with that recently presented.[1] The harmonic force field has been calculated and will be compared with that of HOCl and with those derived from *ab initio* calculations. Changes in quadrupole coupling with the BrO stretch and DOBr bend have been determined.

[1] E. A. COHEN, G. A. MCRAE, T. L. TAN, R. R. FRIEDL, J. W. C. JOHNS AND M. NOËL, *J. Mol. Spectrosc.* **173**, 55 (1995).