THE ν_1 BANDS OF $Br^{14}NO_2$ AND $Br^{15}NO_2$ AROUND 7.8 μm STUDIED BY HIGH-RESOLUTION FOURIER-TRANSFORM ABSORPTION SPECTROSCOPY

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Nitryl bromide ($BrNO_2$) is a molecule of atmospheric interest. It is probably formed by heterogeneous reactions on polar stratospheric clouds and on sea-salt aerosol particles in the marine troposphere[a], and by gas-phase reactions of bromine atoms with NO_2[b]. $BrNO_2$ is chemically unstable and difficult to synthesize. From the spectroscopic point of view, $BrNO_2$ is a heavy asymmetric top with small rotational constants and some low-energy fundamental vibrations, leading to a rather congested spectrum in the mid-infrared. Recently, we have presented the first high-resolution infrared spectrum of gaseous $BrNO_2$ in the region of the *b*-type ν_4 bands around 6 μm.[c] The ground-state rotational constants of $BrNO_2$ were determined from the infrared spectra using ground-state combination differences. Although it is possible to estimate the molecular structure using the ground-state rotational constants of $^{79}BrNO_2$ and $^{81}BrNO_2$, the small displacement of the center-of-mass between these isotopomers causes a strong correlation between the Br-N bond length and the O-N-O angle. Therefore, high-resolution absorption spectra of the *a*-type ν_1 bands of $Br^{14}NO_2$ and $Br^{15}NO_2$ were recorded with a spectral resolution of 0.002 cm^{-1} using the Bruker IFS-120HR FTS at the University of Hannover. The bands were analyzed using a Watson-type *A*-reduced Hamiltonian in the I^r representation[d]. The analysis confirms the rotational constants derived from line assignments in the ν_4 bands, and allows for an accurate determination of the ground-state substitution structure of $BrNO_2$.

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[b] W. B. DeMore et al., *JPL Publ.* **97-4** (1997)
[c] J. Orphal, A. Frenzel, H. Grothe, B. Redlich, D. Scheffler, H. Willner, and C. Zetzsch, submitted to *J. Mol. Spectrosc.* (1998)
[d] J. K. G. Watson, in *Vibrational Spectra and Structure* (Ed. J. R. Durig), 1–89, Elsevier, Amsterdam (1977)