Observations of the diurnal variations of BrO and OClO at McMurdo Station, Antarctica (78S)

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Observations of the diurnal variations of OClO and BrO during austral spring, 1987 using long-path visible and near-ultraviolet absorption spectroscopy are presented and compared to simplified model calculations. It is shown that care must be taken to compare model calculations and measurements along the line of sight of the instrument. Evening twilight observations of OClO are shown to be broadly consistent with current photochemical schemes, assuming ClO and BrO levels near 50 mb of about 0.5 ppbv and 7 pptv, respectively, throughout the observing period from late August to mid-October. Nighttime observations of OClO obtained using the moon as a light source display evidence for growth through the night in late-August, but not in late-September. Further, the observed morning twilight OClO abundances are in agreement with model calculations in late August, but generally fall below in late September and October. Observations of BrO in mid-September systematically show far greater evening twilight than morning twilight abundances. It is shown that the diurnal variations of BrO and OClO in mid-September and October can be explained by formation of the $BrONO_2$ reservoir species at night, although other reservoir species with comparably long lifetimes could also explain the observations. If formation of $BrONO_2$ is the correct explanation for these data, the observations suggest that NO_2 levels in the antarctic lower stratosphere are on the order of a few pptv or less in late August, a few tens of pptv in mid-September, and a few hundred pptv in October. Constraints on the coupled nitrogen-halogen chemistry of the austral spring season revealed by the observed diurnal variability of OClO and BrO will be discussed.