Observation of a New Absorption Band of HOBr and Its Atmospheric Implications

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A new absorption band of HOBr centered near 440 nm is detected by monitoring the yield of OH radicals as the wavelength of an excitation laser is scanned over the region from 440 to 650 nm. The band is believed to arise from excitation to a triplet state of HOBr, and although its peak absorption cross section is fairly modest, $\sigma_{max} \sim 9 \times 10^{-21}$ cm², its influence on determining the photochemical lifetime of HOBr is large due to its proximity to the peak of the solar actinic flux. Preliminary estimates suggest that inclusion of absorption by this new band system will shorten the photochemical lifetime of tropospheric HOBr in the polar regions by a factor of 2 compared to the recently recommended value based on the near-UV absorption bands alone.

Introduction

The chemistry and photochemistry of chlorine-containing compounds has been the subject of numerous studies over the past few years primarily due to the role they play in the catalytic destruction of ozone.¹ Recent measurements indicate that on a per molecule basis, the ozone depletion potential for bromine is even greater than that of chlorine.^{2,3} In addition several recent studies have linked bromine directly to ozone destruction cycles in various regions of the earth's atmosphere.^{4–7} A potentially important bromine containing species is hypobromous acid (HOBr). HOBr is produced in the atmosphere both by the gas-phase reaction^{5,8} of HO₂ with BrO and in regions of low sunlight, such as the night time stratosphere, by heterogeneous reactions involving the hydrolysis of BrONO₂ on aerosol particles:^{7,9}

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (gas-phase) \tag{1}$$

$$BrONO_2 + H_2O \rightarrow HOBr + HNO_3$$
 (heterogeneous) (2)

The importance of hypobromous acid in influencing stratospheric ozone concentration arises in part from its involvement in the following catalytic cycle for ozone destruction:^{2,4,6}

$$BrO + HO_2 \rightarrow HOBr + O_2$$
 (3)

$$HOBr + h\nu \rightarrow OH + Br \tag{4}$$

$$Br + O_3 \rightarrow BrO + O_2 \tag{5}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{6}$$

net:
$$2O_3 \rightarrow 3O_2$$
 (7)

In addition, heterogeneous reactions of HOBr on aerosol particles with HCl can also generate BrCl which when subsequently photolyzed provides an additional source of radicals for ozone depletion:^{10,11}

$$HOBr + HCl \rightarrow BrCl + H_2O$$
 (heterogeneous) (8)

$$BrCl + h\nu \to Br + Cl \tag{9}$$

Another important consequence of the above reaction schemes (see reactions 4, 6, 8, and 9) is that HOBr can couple ozone destruction cycles involving bromine with those involving chlorine and OH radicals.¹⁰ The extent of this coupling, in part, is determined by the concentration of HOBr in the atmosphere which in turn is controlled by its photolysis rate. Photochemical data on HOBr are sparse, although recent studies by Orlando and Burkholder have provided an accurate measurement of its UV absorption bands in the region 240-400 nm.¹² As is apparent from their work, a serious difficulty in recording the electronic absorption spectrum of HOBr is interference from strong absorption bands of Br₂O and Br₂ that appear, respectively, in the UV and visible regions of the spectrum. These species are typically present in large concentrations as part of the source chemistry required to generate HOBr and, thus, their contribution to the absorption signal is difficult to eliminate. By careful background subtraction, however, Orlando and Burkholder were able to minimize this problem and obtain absorption cross-section data even for overlapping spectral regions.12

An alternate method of recording an absorption-like spectrum, which works well for molecules that dissociate, is to monitor the yield of a particular photofragment while scanning the wavelength of the photolysis light source. This approach generates an "action" spectrum whose information content complements that obtainable through direct absorption spectroscopy. Whereas the absorption spectrum reveals the total probability for photoabsorption, the action spectrum provides the component of this probability which leads to formation of the interrogated product (i.e., a partial cross section). Thus, cross sections obtained by the two methods will be equal when the quantum yield for forming the detected product is unity.

In this letter we report the observation of a new absorption band of HOBr centered in the region of 440 nm. The spectrum is obtained by monitoring the yield of OH fragments via laserinduced fluorescence (LIF) as the excitation laser is scanned over the HOBr absorption features occurring between 440 and 650 nm. Apparently, HOBr photodissociates over much of this wavelength region. Since the action spectrum relies on detecting laser induced fluorescence of the OH fragments, we greatly minimize interference due to Br_2 absorption which also occurs in this spectral window. We find that the new absorption band makes a significant contribution to determining the atmospheric lifetime of HOBr due to the fact that the peak of the solar radiation flux occurs in the visible. As we show below,

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absorption cross-section estimates based on the assumption that the quantum yield for OH production at 355 and 510 nm are unity suggest that the lifetime of tropospheric HOBr will be shortened by a factor of 2 at the polar latitudes compared to recent estimates based on the absorption data for the UV bands alone.

Experimental Method

The experiments on HOBr are carried out using a slight modification of the apparatus used in our earlier work on HO_2 .¹³ We generate HOBr in a manner similar to that described in the literature.^{12,14,15} Briefly, water vapor and Br₂ are flowed through two separate ports at one end of a glass column (1.5 cm diameter \times 35 cm length) packed with a mixture of yellow HgO (reagent grade) and 6 mm diameter glass beads. The beads allow for a loose packing of the HgO powder and thus ensure uniform flow of the reagent gases through the column. The other end of the column is connected to the glass photolysis cell, and the mixture of reactants and HOBr products continuously flows through the cell and into a partially throttled mechanical vacuum pump. The pressure in the cell is maintained between \sim 80 and 700 mTorr depending on the measurement. To regulate its vapor pressure, the reservoir containing Br_2 is kept at a temperature of $-10 \text{ }^{\circ}C$ using a salt-ice bath. All components coming in contact with the reagents prior to entering the cell are made of either glass or Teflon in order to avoid potential catalytic loss of HOBr on metal surfaces. Under typical flow conditions, the HgO column is able to generate sufficient yields of HOBr to last about a week before requiring refilling.

Photolysis radiation is generated by using the third harmonic of a Nd:Yag laser (Spectra Physics GCR-270) to pump an Optical Parametric Oscillator (OPO, Spectra Physics MOPO-730). The signal beam from the OPO laser provides continuously tunable radiation from 440 to 650 nm with a bandwidth of ~ 0.2 cm⁻¹ and pulse energies ranging from 10-60 mJ across its tuning range. The unfocused OPO beam is directed into the photolysis cell through a set of baffled sidearms and travels collinearly relative to the probe laser. The OH photofragments are detected via the A-X transition at \sim 308 nm using LIF.¹³ Radiation in this wavelength region is generated by frequency doubling the output of a second Nd:Yag laser (Continuum NY81-20) pumped dye laser (Continuum ND60) having a bandwidth of 0.12 cm^{-1} in the UV. Both photolysis and probe lasers are operated at 20 Hz with the delay between them being variable from 20 ns to 1.0 μ s depending on the particular measurement.

The fluorescence excited by the probe laser is imaged onto a photomultiplier tube (EMI 9635QB) using an f/1 lens system and a gated integrator captures the resulting signal for subsequent storage on a personal computer. A colored glass filter (Corning 7-54) and a 310 nm interference filter (Acton Research) are used to reduce scattered light. The photolysis laser energy is measured as the beam exits the photolysis cell using a volume absorber laser power meter while the probe laser energy is monitored using a photodiode. The power readings for both lasers are simultaneously recorded along with the OH fluorescence signal for purposes of normalization.

In this study we generate two types of action spectra. A nascent action spectrum is generated by monitoring laser induced fluorescence from an unrelaxed OH quantum state as the photolysis laser is scanned over its tuning range from 440 to 650 nm. For these experiments the pressure in the cell is maintained around 80–100 mTorr and the time delay between the lasers set between 20 and 30 ns to prevent interference from collisions and secondary chemistry. In a separate experiment



Figure 1. (a) LIF spectrum of OH generated from HOBr photolysis at 510 nm. The first few transitions of the Q_1 branch are labeled. (b) Dependence of the OH LIF signal on the photolysis laser energy. The energy of the photolysis laser is measured after it exits the reaction cell.

we also record action spectrum by monitoring signal from a thermally relaxed product state distribution. For this study 600– 700 mTorr of nitrogen buffer gas is added to the cell containing 50–60 mTorr of HOBr/H₂O/Br₂ reaction mixture and the time delay between the photolysis and probe lasers increased to 1.0 μ s in order to ensure thermalization of the OH internal degreesof-freedom and quenching of Br₂ background fluorescence. These same conditions, long time delay and high pressure, are also utilized in determining the relative cross section of the new absorption band, where the yield of thermalized OH resulting from 510 nm photolysis is compared with that from the photolysis of HOBr at 355 nm.

Results and Discussion

Recent theoretical and experimental data suggest that the heat of formation of HOBr (at 0 K) is -11.8 kcal/mol.^{16,17} Thus, on the basis of its thermochemistry we expect photons of wavelength shorter than ~580 nm will be required to break the HO–Br bond. Figure 1a shows an LIF spectrum generated by setting the photolysis laser at 510 nm while the probe laser is scanned over the 308–310 nm range. The observed peaks are assigned to OH radicals formed in their ground vibrational state based on the classic work of Dieke and Crosswhite.¹⁸ No signal from OH (v''=1) is observed.

Several pieces of evidence suggest that the observed OH signal is due to HOBr photolysis. First we find that the signal is present only when both the Br_2 and H_2O flows are

simultaneously on and disappears when either one of the flows is turned off, consistent with the required source chemistry for HOBr production. Using FT-IR spectroscopy, previous investigators have probed the same source chemistry and did not observe any OH-containing compound other than HOBr and H_2O .¹⁹ In addition, we find that the OH LIF signal does not exhibit a buildup time; the signal is maximum when the delay between the photolysis and probe laser is short (20–30 ns) and decreases as the relative time delay between the two lasers is increased. This observation is consistent with the signal being generated by a photodissociation event and not a bimolecular reaction. A power dependence study of the OH LIF signal as a function of the photolysis laser energy indicates a linear relationship consistent with a single photon dissociation (Figure 1b).

We rule out the possibility that the signal is being generated from the photolysis of a complex (e.g., H₂O:Br₂ and H₂O:Br₂O) since at the relatively high temperatures and low pressures used in this study the concentration of such species is expected to be negligible. In addition, the available energy near the long wavelength end of the current study (e.g., $\lambda > 530$ nm) is insufficient to overcome the endothermicity associated with reactions that form OH from these complexes.

Parking the probe laser on the OH $Q_1(2)$ transition while scanning the OPO photolysis laser over its tuning range from 440 to 650 nm generates an "action" spectrum similar to that shown in Figure 2a. This particular unrelaxed action spectrum is derived by taking seven separate scans and averaging them together on 0.5 nm intervals in order improve signal-to-noise and, thus, obtain the composite spectrum shown. Parking the probe laser on the $Q_1(5)$ transition of OH gives rise to an action spectrum similar to that shown for the $Q_1(2)$ transition except with reduced signal-to-noise ratio.

Figure 2b shows a spectrum over the same wavelength region with the probe laser *parked off the OH resonance*. It is clear from comparing Figure 2a and 2b that for photolysis wavelengths shorter than \sim 513 nm the dominant fluorescence signal is generated by OH, whereas for wavelengths longer than this there is an additional source of fluorescence. This background fluorescence is not dependent on the wavelength of the probe laser and appears to be roughly of uniform strength over the 308-309 nm range, independent of whether the probe laser is on or off an OH resonance. However, the background signal does depend on the relative timing of the two lasers and appears only when the OPO is fired before the probe laser. We also find that the fluorescence lifetime of the background signal is noticeably different from that of OH and that it depends on Br₂ being present in the cell but is independent of the H₂O flow. By process of elimination, we attribute this additional fluorescence signal to a two-photon transition in Br_2 . The sharp spectral features seen in Figure 2b as the OPO is scanned suggest that the first step involves excitation of a bound-bound transition (to the $B^3\Pi_{0u}$ state of Br₂) followed by subsequent excitation by the probe laser from the B state to an ion-pair state (most likely the $D^3\Pi_{1g}$ state) from which the molecule fluoresces.²⁰ The lack of background fluorescence to the blue of \sim 513 nm is due to the fact that, although Br₂ absorbs at these wavelengths, the intermediate $B^3\Pi_{0u}$ state dissociates above this limit.

We are able to eliminate the interference due to Br_2 fluorescence completely by increasing the time delay between the photolysis and probe lasers and adding nitrogen buffer gas to quench the Br_2 fluorescence. Figure 3a illustrates a thermalized action spectrum of HOBr generated using high pressure and long time delays, and Figure 3b shows the corresponding



Figure 2. (a) Composite action spectrum of HOBr with the probe laser parked on the $Q_1(2)$ transition of OH. These spectra are recorded at total pressure of 100 mTorr, with the delay between photolysis and probe lasers set to 30 ns. (b) Variation in the two-color Br₂ background fluorescence signal with the wavelength of the photolysis laser. The wavelength of the probe laser is fixed at ~308 nm but off any OH transitions in the region. The cell pressure and time delay between the lasers are the same as in part (a).

background signal with the probe laser parked off the OH resonance. We see that the Br_2 background fluorescence is completely eliminated and that the relaxed action spectrum is slightly blue shifted compared to the nascent spectrum shown in Figure 2a. The absence of any structure in the action spectrum in Figure 3a and the observation of OH radicals, confirms that HOBr dissociates rapidly at these wavelengths to give OH + Br. The thick line through the experimental data in Figure 3a is a fit to the measured action spectrum using the following functional form:

$$I(\nu) = I_0(\nu/\nu_0) \exp[-(\nu - \nu_0)^2 / (\Delta \nu)^2]$$
(10)

The rationale for using such a function is that if we treat the triatomic HOBr molecule as a pseudodiatomic system, then via the reflection principle²⁰ the absorption spectrum simply maps out the square of the ground-state vibrational wave function along the Br–O coordinate in the Franck–Condon region, and thus should resemble in frequency space a Gaussian function multiplied by the frequency. The fitted function allows us to estimate the full impact of this new band system by extrapolating its value beyond the region of our current measurements. The best-fit parameters from the simulation are $I_0 = 8.85 \times 10^{-21}$ cm², $\nu_0 = 22725$ cm⁻¹, and $\Delta \nu = 2664$ cm⁻¹.



Figure 3. (a) Action spectrum of HOBr with the probe laser parked on the Q₁(2) transition of OH. This spectrum was recorded with the total pressure increased to ~700 mTorr using nitrogen buffer gas and the time delay between photolysis and probe lasers increased to one microsecond. The thick line in the figure represents a best fit to the data using the functional form $I(\nu) = I_0(\nu/\nu_0)\exp[-(\nu - \nu_0)^2/(\Delta\nu)^2]$. (b) Variation in the two-color Br₂ background fluorescence signal with the wavelength of the photolysis laser under conditions of high pressure and long time delay. The probe laser is fixed at ~308 nm but off any OH transitions in the region. The cell pressure and time delay between the lasers are the same as in part (a).

We obtain information regarding the cross section associated with the new absorption band by comparing relative yields for OH production at 355 and 510 nm under conditions where the nascent fragment product state distributions are thermalized. From thermodynamic considerations, OH + Br is the only product channel open at 510 nm. Assuming that the quantum yield for OH production is also unity at 355 nm and using the reported absorption cross section for this wavelength,¹² we estimate the cross section for the new band from the ratio of OH yields at 355 vs 510 nm and, as a further consistency check, we also use the ratio of OH yields at 355 vs 480 nm. The assumption of a unit quantum yield for OH production at 355 nm is not too unreasonable since photodissociation experiments on HOBr at 363 nm indicates that for this wavelength, the OH channel accounts for >95% of the dissociation.²²

Figure 4 displays the composite data for both the near-UV and visible absorption bands of HOBr. The impact of the new absorption feature on the atmospheric lifetime of HOBr is best explored by calculating its photodissociation rates. On the basis of the calculated actinic solar flux at the earth's surface,²² the UV data of ref 12 results in a photolysis rate of $7.4 \times 10^{-4} \text{ s}^{-1}$, which corresponds to a lifetime of 22 min at a 30° solar zenith angle based on unit quantum yield for photolysis. If the present visible absorption band, modeled using eq 10, is included along with the previously reported UV bands, then for the composite



Figure 4. Composite spectrum of the visible and near-UV absorption bands of HOBr. The solid line represents the best fit to our thermalized action spectrum using eq 10, extrapolated to 370 nm. The dashed line represents the fit given by Orlando and Burkholder¹² to their UV absorption data.

UV-visible absorption band system the photolysis rate increases to $1.1 \times 10^{-3} \text{ s}^{-1}$, corresponding to a lifetime of ~15 min. At a 78° solar zenith angle, appropriate for the Arctic spring, a photolysis rate of $1.2 \times 10^{-4} \text{ s}^{-1}$ (140 min lifetime) is estimated with the UV bands alone while this rate increases to 2.2×10^{-4} s⁻¹ (76 min lifetime) with the inclusion of the 440 nm band. Models dealing with sudden ozone depletion of the Arctic troposphere^{7,23} specifically mention uncertainties in the HOBr photolysis rates as hampering their assessment of the contribution of bromine chemistry to Arctic ozone loss. The current increase in HOBr photolysis rate may have important implications for these models.

In addition to affecting models of bromine chemistry in the Arctic troposphere, the current results may also influence models which attempt to account for the OH burst seen in the lower stratosphere.²⁴ Recent measurements of the diurnal variation in OH radical concentrations in the lower stratosphere indicate a rapid rise in OH concentration during sunrise which they attribute to the photolysis of a species that absorbs light at wavelengths longer than 320 nm. It has been hypothesized that photolysis of HNO₂, at roughly the 12 parts per trillion level, generated at night through heterogeneous decomposition of HNO₄, is the source of the OH spike. However in light of the present results, if the concentration of HOBr is sufficiently high, then photolysis of HOBr in the visible can also contribute to the OH spike, and our data suggest that a more careful assessment of this possibility is needed.

Although the dynamics of HOBr dissociation will be reported in a separate paper,¹⁷ we briefly mention that Doppler/ polarization spectroscopy of the OH fragments indicates a nonisotropic velocity distribution consistent with rapid dissociation resulting from excitation to a repulsive excited electronic state. In addition, comparison of OH Doppler line profiles resulting from dissociation within the visible band with those resulting from 355 nm photolysis shows clear differences (see Figure 5) which confirms that the excited electronic state responsible for the visible band is different from that accessed at 355 nm. Recent ab initio calculations on HOBr using the MRCISD method indicate that in the wavelength region under consideration, there are no singlet states which can account for the observed band system.²⁵ However, considering the manifold



Figure 5. Nascent Doppler profiles of the OH $P_1(4)$ transition resulting from HOBr photolysis. In both cases the probe and photolysis laser are propagating perpendicular to one another, with their respective electric field vectors polarized in the plane formed by their propagation directions. (a) Photolysis at 450 nm near the peak of the visible band. (b) Photolysis at 355 nm near the peak of the first UV band. The solid lines represent fits to the data.

of triplet states, the calculations reveal the existence of a dissociative triplet state at 2.6 eV. We believe that the present absorption band is due to transitions from the ground X^1A' electronic state to this triplet state of HOBr.

In conclusion we note that a new absorption band of HOBr has been uncovered which doubles its tropospheric photolysis rate at the polar regions (more specifically at ground level with a solar zenith angle of 78°). The band is believed to arise from excitation to a dissociative triplet electronic state. The present results, in addition to providing information on HOBr and demonstrating the utility of an "action" spectrum, suggests that as we investigate the atmospheric photochemistry of the heavier halogen (Br and I) containing compounds, the role of singlet triplet transitions, which are nominally "forbidden", need to be carefully considered as many of these transitions can occur with nonnegligible intensity in the visible region of the solar spectrum.

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