

Temperature-Programmed Desorption and Reflectance Absorption Infrared Spectroscopy of H₂O:HBr Thin Films of Varying Stoichiometry from <1:1 to 5:1

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Temperature-programmed desorption (TPD) and reflection absorbance infrared spectroscopy (RAIRS) were used to study H₂O:HBr thin films of varying stoichiometry from <1:1 to 5:1. These films were deposited on a Ag(110) crystal at $T = 100$ K. The TPD data showed a single desorption peak near 180 K in the H₂O⁺ ($m/e = 18$) mass channel for all of the films investigated. In the HBr⁺ ($m/e = 82$) mass channel, a single desorption peak near 180 K was observed for films with a H₂O:HBr stoichiometry $\geq 3:1$, indicating sublimation of the H₂O:HBr film. For films with a H₂O:HBr stoichiometry $< 3:1$, HBr desorption began at temperatures as low as 125 K. The HBr desorption peak was broad and continuous until the entire H₂O:HBr film desorbed near 180 K. RAIR spectra of the H₂O:HBr films were also recorded as a function of film temperature. The infrared data in conjunction with TPD allowed for changes in the spectra to be interpreted in terms of changes in film crystallinity and film composition.

Introduction

In recent years, the impact of heterogeneous reactions of halogen-containing gases on ozone depletion has been the subject of numerous laboratory studies.^{1–5} In particular, heterogeneous reactions on the surface of polar stratospheric clouds (PSC's) including those composed primarily of ice (type II PSC's) have been investigated.¹ PSC surfaces provide a medium for the conversion of stable halogen reservoir molecules into more photochemically active molecules. Hydrogen halides are important reservoir molecules, and while there have been many studies of HCl adsorption on ice,^{1–10} there have been fewer for other hydrogen halides such as HBr^{11–16} and HI.^{17–19}

Infrared spectroscopy has been a useful tool for studying the adsorption and interaction of hydrogen halides in and on ice. Over 25 years ago, Gilbert and Sheppard investigated the transmission infrared spectra of various condensed HCl and HBr water mixtures.²⁰ They found marked spectral changes with temperature and interpreted these data as compositional changes in the film. In their experiments, premade gas mixtures were admitted into a gas cell and condensed on liquid nitrogen cooled KBr or CsI flats. Temperature-dependent studies in conjunction with premade gas mixtures of differing composition were used to assign the spectra to crystalline forms of various hydrogen halide hydrates. Many current FT-IR studies base their assignments on those of Gilbert and Sheppard.

More recently, Delzeit et al.²¹ published infrared data for a series of amorphous and crystalline HBr and HCl hydrates and offered a new interpretation of the Gilbert and Sheppard data. In these experiments, amorphous films were deposited at 85 K in a closed cell. The amorphous nature was confirmed by carrying out some experiments on films deposited at much lower temperatures near 15 K. Upon heating an amorphous 1:1 (H₂O:HBr) film deposited at 85 K, spectral changes were observed. These changes were characterized using several premade H₂O:HBr gas mixtures (a 1:1 deposited at 15 K, a slightly HBr-rich

1:1 film deposited at 85 K, and 2:1, 4:1, and 6:1 deposited at 80 K). The spectra were interpreted as conversion of the amorphous 1:1 film into a crystalline 1:1 film at 100 K, 2:1 film at 195 K, and a 4:1 film at 215 K.

In a recent infrared study focused on the atmospheric implications of HBr adsorption as well as other hydrogen halides on ice, H₂O:HBr films with stoichiometries of 2:1, 3:1, 4:1, and 6:1 were deposited at 140 K.¹⁵ These films were characterized as amorphous. Spectral changes after subsequent heating of these films to 160 K were interpreted as an amorphous to crystalline transition without change in stoichiometry.

In an attempt to more clearly separate spectral changes due to film structure and those due to film stoichiometry, thin H₂O:HBr films of varying composition were investigated with reflectance absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD). Instead of assuming a film stoichiometry based on changes in the RAIR spectra, calibrated mass spectral data was used as an independent method for determining initial film stoichiometry and changes in stoichiometry as a function of temperature. This combined approach allowed for a more careful determination of the cause of spectral changes, i.e., whether the changes were due to changes in film structure and/or composition.

Experimental Section

Experiments were carried out in an ultrahigh-vacuum (UHV) chamber with a base pressure of $(1–5) \times 10^{-9}$ Torr during experiments. The UHV chamber is equipped with a cylindrical mirror analyzer for Auger electron spectroscopy, quadrupole mass spectrometer for TPD and residual gas analysis, an ion sputtering gun for sample cleaning, and three variable leak valves for introducing gases into the chamber. A Ag(110) substrate was mounted in the UHV chamber on a tantalum cup attached to a liquid nitrogen cooled Cu block. The temperature of the Ag(110) substrate during experiments was measured by a chromel–alumel thermocouple to be 100 K.

TPD experiments were performed by heating the Ag(110) substrate resistively at a rate of 1.5 K/s. A UTI-100C quadrupole

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mass spectrometer (QMS) with a mass range from $m/e = 1$ to 300 was interfaced to a 486 PC through an National Instruments AD/DA board (AT-MIO-16H-9).

A Mattson 6021 Galaxy FT-IR spectrometer equipped with external beam capabilities and a narrow-band mercury–cadmium–telluride (MCT) detector was used for reflectance infrared measurements. The lower limit of the spectral range of the instrument was limited to $\sim 750\text{ cm}^{-1}$ by the MCT detector. Each absorbance spectrum was acquired by summing 1000 sample scans at an instrument resolution of 4 cm^{-1} and referencing to background scans of the clean Ag(110) substrate acquired under the same conditions.

Some experiments were carried out at lower temperatures. These experiments required using a closed-cycle refrigerator with a CaF₂ flat mounted in a stainless steel sample holder. The temperature of the CaF₂ flat was measured using an iron doped gold/chromel thermocouple sandwiched between the CaF₂ flat and the sample holder. In this experimental arrangement, FTIR data were recorded in the transmission mode.

Pure ice films thicknesses were estimated from the calibration procedure described by Foster et al.^{9,14} In their procedure, optical interference was used to calibrate H₂O exposures in terms of ice thickness. It was determined that a 30 langmuir exposure produced a 122 Å film. Using their calibration, ice thicknesses are reported in angstroms.

The stoichiometry of the H₂O:HBr films was determined from mass spectral data including residual gas analysis (RGA) during dosing and TPD of the entire film. Calibration of the QMS was done by taking into account the sensitivity of both the ion gauge and QMS with respect to each gas.¹⁴ The ion gauge sensitivity was determined by measuring the ion gauge reading after backfilling the chamber with a known pressure of each gas. Absolute gas pressures were determined using a sensitive capacitance manometer that could be used for calibrations down to 1×10^{-6} Torr. These data were extrapolated to lower pressures, and the QMS sensitivity measured relative to the ion gauge sensitivity was then determined. The QMS was calibrated for the two parent ions H₂O⁺ ($m/e = 18$) and H⁸¹Br⁺ ($m/e = 82$). Because bromine has two isotopes, ⁷⁹Br and ⁸¹Br, of nearly equal abundance, a factor of 2 was taken into account for calibration of the total amount of HBr. This calibration allowed the H₂O:HBr ratio of premade gas mixtures to be determined from the residual gas analysis (RGA), and the resulting film stoichiometry for each film was calculated from the integrated areas of the TPD curves. As some of the TPD data sets had sloping backgrounds, each data set was baselined so as to avoid any errors in calculations.

HBr (99.999%) was obtained from Matheson Gas Products and used without further purification. The H₂O used throughout the course of these experiments was Millipore filtered and subjected to several freeze–pump–thaw cycles prior to use. Gas mixtures were allowed to passivate in the manifold over overnight before fresh mixtures were made the following morning.

Results

Temperature-Programmed Desorption of H₂O and H₂O/HBr Thin Films. To aid in the interpretation of the TPD data for thin films deposited from premade H₂O:HBr gas mixtures, a series of TPD experiments were performed on pure ice films approximately 140 Å thick deposited on Ag(110) at 140 K and then exposed to HBr at 140 K. As shown recently, adsorption and diffusion of HBr in the ice film are facile at 140 K compared to lower temperatures.¹⁴ Pure ice films showed a desorption peak

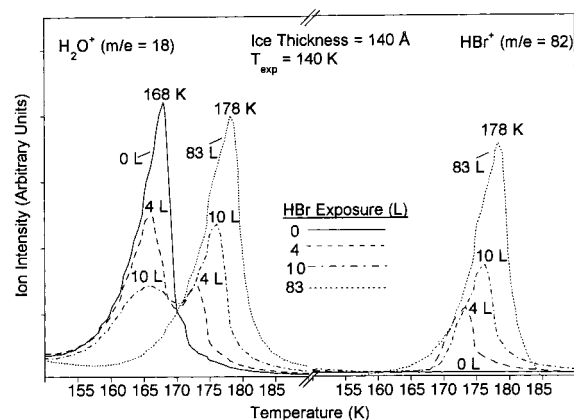


Figure 1. Representative TPD curves for H₂O⁺ and HBr⁺, $m/e = 18$ and 82, for ice films 140 Å thick deposited at 140 K and exposed to HBr at 140 K. HBr exposures are given in units of langmuirs (L).

TABLE 1: A Comparison of Film Stoichiometry of Determined by RGA during Gas Deposition and from TPD Analysis of the Deposited Films

Ratio from RGA	Ratio from TPD
$0.10 \pm 0.10:1$	$0.3 \pm 0.10:1$
$1.6 \pm 0.20:1$	$1.2 \pm 0.2:1$
$2.0 \pm 0.20:1$	$2.0 \pm 0.2:1$
$3.0 \pm 0.2:1$	$3.3 \pm 0.2:1$
$4.1 \pm 0.3:1$	$4.8 \pm 0.3:1$

near 168 K for H₂O⁺ ($m/e = 18$), and as expected, no desorption feature was seen in the HBr⁺ ($m/e = 82$) mass channel. Upon exposure to HBr, the pure water desorption peak decreased in intensity, and a second peak for H₂O⁺ became apparent near 178 K. After ice was exposed to HBr, desorption was seen in the HBr⁺ channel near 178 K. These data are shown in Figure 1 for a series of HBr exposures to crystalline ice. The presence of desorption peaks in both mass channels, H₂O⁺ and HBr⁺, at the same temperature indicates that these peaks are due to the sublimation of the H₂O:HBr film and that HBr is being incorporated into the film. HBr adsorption into ice films of different thickness provides additional evidence for HBr incorporation into the ice film as the amount of HBr incorporated is dependent upon film thickness. Analysis of four ice films exposed to a saturation amount of HBr (exposures >50 langmuirs) yielded a film stoichiometry of $3.9 \pm 0.1:1$ (H₂O:HBr). The calibration procedure for determining film stoichiometries is described in the Experimental Section.

Following HBr adsorption experiments on ice at 100 K, premade gas H₂O:HBr mixtures were deposited on a Ag(110) crystal held at 100 K. It should be noted that although pure H₂O films can be deposited on Ag(110) at this temperature, pure HBr films cannot; i.e., the sublimation temperature of HBr is below 100 K. However, premade gas mixtures of H₂O:HBr can be readily deposited on Ag(110) at 100 K, and as shown above HBr uptake by pure ice films can also take place at this temperature. Premade gas mixtures were characterized during film deposition by RGA for the duration of the deposition period. Film stoichiometries were also analyzed by TPD following deposition. There were some differences between the stoichiometries determined from gas-phase analysis compared to that of the film determined from the TPD data (see Table 1), although, most of these differences are within the experimental error of the data. It is important to note that there was only agreement between the RGA analysis and the TPD analysis if the UHV chamber was passivated for several days by exposing the stainless steel walls of the UHV chamber and the gas handling line to HBr. Without passivation, the stoichiometries

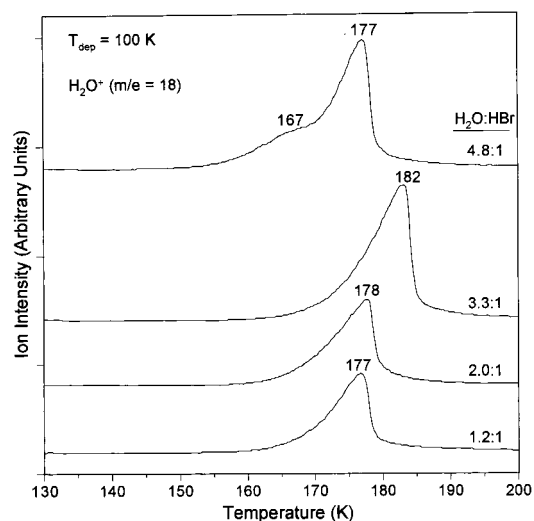


Figure 2. Representative TPD curves for H_2O^+ ($m/e = 18$) for H_2O :HBr films deposited from premade H_2O :HBr gas mixtures at 100 K. Film compositions given in the figure are those determined from TPD analysis of the film (see text for further discussion).

between the RGA and TPD could differ significantly. In particular, films analyzed by TPD contained much lower amounts of HBr than the RGA showed.

The TPD spectra of films deposited from premade gas mixtures showed a single desorption peak in the water channel for film stoichiometries of H_2O :HBr ranging from $<1:1$ to $\sim 4:1$. Representative desorption curves for 1.2:1, 2.0:1, and 3.3:1 are shown in Figure 2. The desorption rate maximum ranged from 177 to 182 K for these films and is a result of differing film thicknesses, with the 3.3:1 film being approximately 3 times as thick as the others. Also shown in Figure 2 is the desorption data for a film of stoichiometry $>4:1$. Films of stoichiometry $>4:1$ show two desorption features. A small desorption feature at lower temperatures consistent with water desorption from regions of the film that contain little or no HBr and a desorption feature from regions that contained HBr. The desorption kinetics of the lower temperature feature is similar to that observed for pure water films, and the higher temperature feature is similar to that observed for H_2O :HBr films with stoichiometries ranging from $<1:1$ to $\sim 4:1$.

Representative desorption curves for HBr evolution from H_2O /HBr films deposited at 100 K are shown in Figure 3. For films of stoichiometry $>3:1$, little HBr desorption is seen below ~ 160 K. Sometimes a small desorption feature was observed at ~ 140 K that resulted in a change in film stoichiometry of $<10\%$. The temperature at which this small amount of HBr desorbs from films of stoichiometry $>3:1$ corresponds to the amorphous/crystalline ice phase transition temperature and may be related to a similar phase transition for the H_2O :HBr film. For these films HBr and H_2O desorption occurs simultaneously near $T = 180$ K. Thus, desorption is due to sublimation of the H_2O :HBr film.

For films of stoichiometry $<3:1$, HBr desorption occurs at lower temperatures and over a much greater temperature range. For films rich in HBr with stoichiometries $<1:1$, HBr desorption from the film is seen at temperatures as low as 125 K. For films of stoichiometries near 1:1 and 2:1, the threshold for HBr desorption is shifted to 132 and 140 K, respectively. Desorption of HBr from these films continues as the film is warmed until the entire film has desorbed.

The H_2O :HBr stoichiometry of the film was calculated as a function of temperature for films of initial stoichiometry $<1:1$,

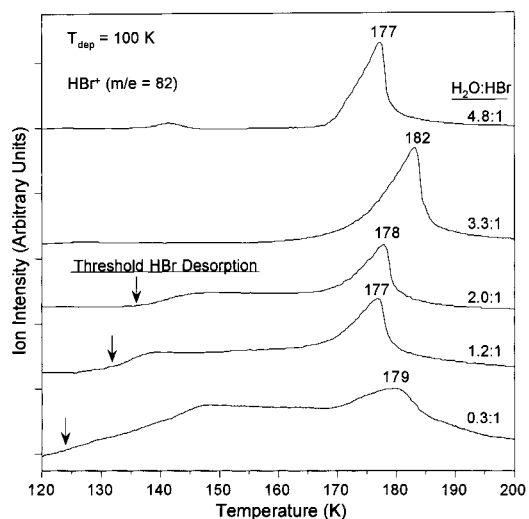


Figure 3. Representative TPD curves for HBr^+ ($m/e = 82$) for H_2O :HBr films deposited from premade H_2O :HBr gas mixtures at 100 K. Film compositions given in the figure are those determined from TPD analysis of the film (see text for further discussion).

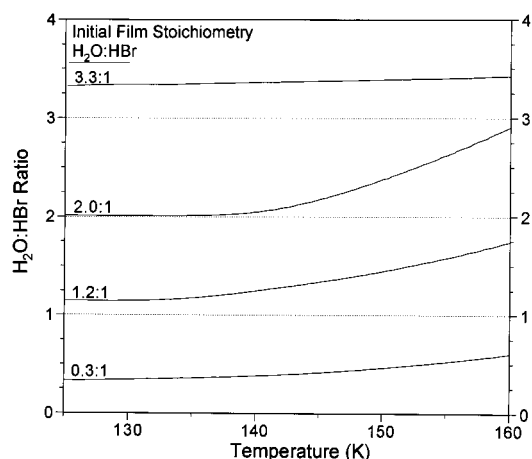


Figure 4. Changes in film stoichiometry as a function of temperature for H_2O :HBr films of initial stoichiometry $<1:1$, 1.2:1, 2.0:1, and 3.3:1. Film stoichiometries at each temperature T_i were calculated from eq 1.

$\sim 1:1$, $\sim 2:1$, and $\sim 3:1$. The stoichiometry at each temperature was determined from TPD data using eq 1:

$$(\text{H}_2\text{O}:\text{HBr})_{T_i} = \frac{\text{total H}_2\text{O desorbed} - \text{fraction of H}_2\text{O desorbed from } T_0 \text{ to } T_i}{\text{total HBr desorbed} - \text{fraction of HBr desorbed from } T_0 \text{ to } T_i} \quad (1)$$

where T_0 is the temperature at the onset of desorption and T_i is any subsequent temperature above T_0 . The film stoichiometry as a function of temperature, i.e., T_i versus H_2O :HBr, is plotted in Figure 4. The 0.3:1 film shows a smooth change in stoichiometry beginning at approximately 125 K. This film has $\sim 1:1$ stoichiometry prior to total desorption. The 1.2:1 film does not begin to change stoichiometry until after approximately 135 K. About 50% of the HBr desorbs from the film prior to desorption of the entire film, and the 1.2:1 film converts to a film of stoichiometry near 2:1. The film with initial stoichiometry of 2.0:1 begins to lose HBr near 140 K. By 163 K, prior to desorption of the entire film the stoichiometry has changed to H_2O :HBr of 3:1.

The TPD results presented in this section allows for changes in the film stoichiometry as a function of temperature in the

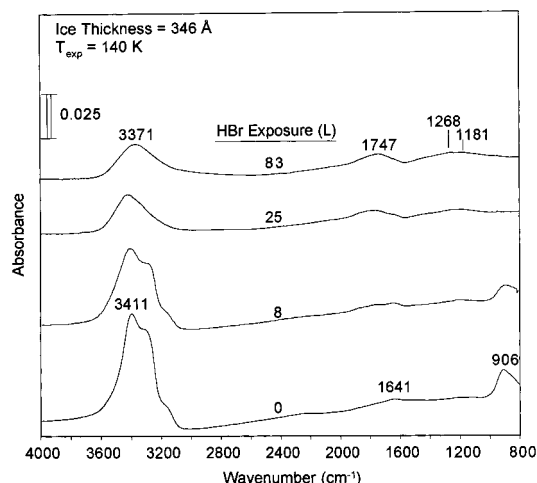


Figure 5. Changes in the RAIR spectra of a 346 Å ice film deposited at 140 K and exposed to HBr are shown. The ice film is saturated with HBr at an exposure of 83 langmuirs. These changes in the infrared spectrum are consistent with the adsorption and diffusion of HBr into the ice film to give H₃O⁺ and Br⁻.

100–165 K region to be determined. These data will be used in the analysis of the temperature-dependent RAIR spectra of premixed films deposited at 100 K.

Reflectance Absorption Infrared Spectra of H₂O and H₂O/HBr Thin Films. In some initial experiments, RAIR spectra were recorded for HBr adsorption in ice at 140 K. Changes in the RAIR spectra of a 346 Å thick ice film deposited at 140 ± 3 K and exposed to HBr at 140 K are shown in Figure 5. Initially at low exposures of HBr, the bending mode of water²² at 1641 cm⁻¹ decreased in intensity while another band grew in near 1747 cm⁻¹. This new band has been previously assigned to the bending mode of H₃O⁺ and shows that HBr ionizes in the film to give H₃O⁺ and Br⁻.^{20,21} The ν₇ frustrated rotation of the water molecules in ice, observed at 906 cm⁻¹,²² disappears upon exposure to HBr. The changes observed in the OH stretching region are also significant. Initially, a band is seen at 3411 cm⁻¹ with two shoulders of lower intensity, consistent with a crystalline ice sample.^{23,24} After exposure to HBr, the band in the OH stretching region decreases in intensity and forms a slightly asymmetric band single band which shifts to lower wavenumbers with a frequency of 3371 cm⁻¹ after saturation of the film. As noted by Barone et al.,¹⁵ the ratio of the integrated absorbance of the OH stretching mode to the bending mode decreases significantly for ice films exposed to HBr compared to the case of pure ice films. In addition to the changes already noted, there are two broad bands that grow in at 1268 and 1181 cm⁻¹. The breadth of these features and the temperature-dependent RAIR spectra to be discussed in the next section indicate that this film is amorphous in nature. Mass-calibrated TPD data presented in the previous section show that this amorphous film is saturated at a H₂O:HBr ratio of 4:1.

H₂O:HBr mixtures with stoichiometries ranging from <1:1 to ~5:1 were then codeposited on Ag(110) at 100 K. Representative RAIR spectra are shown in Figure 6. The films were estimated to be approximately 50–100 Å thick. Film stoichiometries were determined from TPD after recording each of the RAIR spectra. For HBr-rich films of H₂O:HBr stoichiometries <1:1 there is an absorption band at 2591 cm⁻¹ which has been previously observed by Gilbert and Sheppard²⁰ and Delzeit et al.,²¹ this band is assigned in part to molecular HBr hydrogen bonded to H₂O via the complex Br—H...OH₂. At the deposition temperatures used in these studies, i.e., 100 K, this

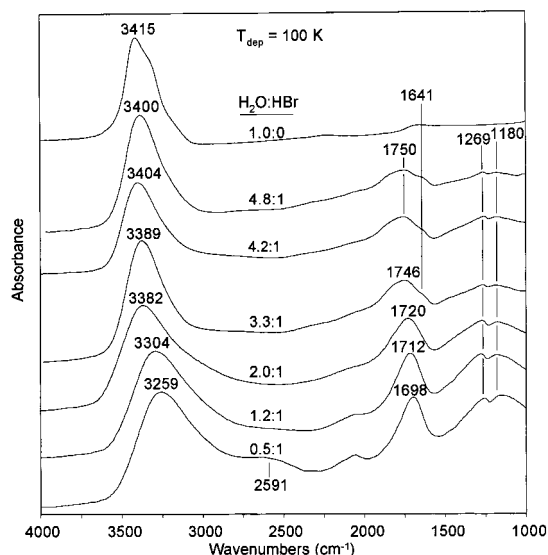


Figure 6. RAIR spectra of H₂O:HBr films deposited from premade gas mixtures at 100 K on Ag(110). Film stoichiometries range from <1:1 to ~5:1 and were determined from TPD analysis of the film after recording a RAIR spectrum. The film of 0.5:1 stoichiometry was determined by RGA analysis of the gas phase during deposition. A pure ice film (labeled H₂O:HBr of 1.0:0) deposited at 100 K is shown for comparison.

band is only observed for HBr rich films with stoichiometries less than 1:1.

To understand the differences between the spectra obtained in this study and those obtained by Gilbert and Sheppard²⁰ and Delzeit et al.,²¹ who performed their experiments below 100 K, a few experiments were carried out at lower temperatures. Lower temperatures were achieved using a closed cycle He refrigerator with a CaF₂ window mounted on the cold tip, allowing transmission FTIR spectra to be recorded. In one experiment an ice film was deposited at 25 K and then exposed to HBr at 25 K. Initially, a HBr multilayer was formed on top of the ice film. This was evidenced by an intense single band at 2445 cm⁻¹, the HBr stretching frequency of solid HBr. Upon warming the film to 90 K, the 2445 cm⁻¹ band decreased in intensity, and a band near 2590 cm⁻¹ became apparent in the spectrum. This new band is associated with HBr hydrogen bonded to H₂O. In another experiment a 0.8:1 film was deposited at 25 K and heated to 90 K. This film also shows an intense band at 2590 cm⁻¹ and is similar to the film formed by depositing an HBr overlayer and heating. These data are consistent with the lower temperature data presented by Gilbert and Sheppard²⁰ and Delzeit et al.²¹ and show that significantly more molecular HBr can be trapped in a film deposited at lower temperatures, giving rise to more of the hydrogen-bonded HBr·H₂O complex.

The other films examined at 100 K all have H₂O:HBr stoichiometries of >1:1 and range from 1.2:1 to 4.8:1. As discussed above, the band near 2590 cm⁻¹ is not present in any of these spectra. The three spectral regions of interest for these films are (i) the OH stretching region between 3000 and 3500 cm⁻¹, (ii) the bending region between 1600 and 1800 cm⁻¹, and (iii) the region between 1100 and 1300 cm⁻¹. RAIR spectra of films with stoichiometries of ~1:1 and 2:1 are very similar and differ mostly in the OH stretching region. For the ~1:1 stoichiometry film the OH absorption maximum is observed at 3304 cm⁻¹. This maximum blue shifts to 3382 cm⁻¹ for a film of 2:1 stoichiometry. For films that contain greater

TABLE 2: Assignment of the RAIR Spectra of Amorphous and Crystalline H₂O:HBr Films of Stoichiometries Ranging from <1:1 to ~5:1

film stoichiometry	film structure	ν_{OH}^a	ν_{HBr}	$\delta_a(\text{H}_3\text{O}^+)$	$\delta(\text{H}_2\text{O})$	$\delta_s(\text{H}_3\text{O}^+), \delta(\text{H}_x\text{O}_y^+)^b$
4.8:1	amorphous	3400	n.o.	1750	1641	1180, 1269
4.2:1	amorphous	3404	n.o.	1750	1641	1180, 1269
3.3:1	amorphous	3389	n.o.	1746	1641	1180, 1269
2.0:1	amorphous	3382	n.o.	1720	n.o.	1180, 1269
1.2:1	amorphous	3304	n.o.	1712	n.o.	1180, 1269
0.5:1	amorphous	3259	2591	1698	n.o.	1180, 1269
4:1	crystalline	3348, 3050	n.o.	1750	n.o.	1005, 1155, 1267
~3:1 ^c	crystalline	3401	n.o.	1707	n.o.	1005, 1155, 1267
~1:1 ^c	— ^d	3400	n.o.	1712	n.o.	1005, 1155, 1267

^a Vibrational frequencies are given in cm⁻¹. ^b Indicates the bending mode of ionic species such as H₃O₃⁺, H₇O₅⁺, and H₉O₄⁺ (see ref 27). ^c For these crystalline films there was simultaneous change in film structure and stoichiometry; therefore, the stoichiometries are estimated from the TPD data presented in Figure 4. ^d The RAIR spectrum of this film was still broad, suggesting that the film had not completely crystallized.

amounts of H₂O with stoichiometries of ~3:1, ~4:1, and ~5:1, this band shifts to higher wavenumbers near 3400 cm⁻¹.

Additional changes are seen in the OH bending mode between 1550 and 1750 cm⁻¹ and the region between 1000 and 1500 cm⁻¹ for films of ~3:1, ~4:1, and ~5:1 stoichiometry. The band at 1712 cm⁻¹ in the ~1:1 film spectra shifts to higher wavenumbers for films that contain greater amounts of H₂O. For a 3:1 film the absorption maximum of this broad band is at 1727 cm⁻¹ for and for films of ~4:1 and ~5:1 stoichiometry is near 1750 cm⁻¹. Also observed in this region, most notably for the ~4:1 and ~5:1 films, is a shoulder near 1641 cm⁻¹ that is observed in the spectrum of pure ice and is assigned to the H₂O bending mode. In the region between 1100 and 1300 cm⁻¹, the bands do not shift in frequency for each film. However, there appears to be a significant decrease in intensity of this broad doublet band relative to other bands in the spectra for films that contain greater amounts of H₂O. The assignments of the RAIR spectra for these amorphous H₂O:HBr films are summarized in Table 2.

Temperature-Dependent Reflectance Absorption Infrared Spectra of H₂O/HBr Films. Several experiments were done to investigate changes in spectral features of films of differing stoichiometry as a function of temperature. For some films, spectral changes were observed when there were no changes in film stoichiometry. Thus, the spectral changes for these films would indicate a change in film structure, i.e., an amorphous to crystalline transition. The top trace of Figure 7 shows the RAIR spectra of such a film. In this experiment, HBr was adsorbed on ice at 140 K. As discussed previously, adsorption of HBr on ice results in an H₂O:HBr stoichiometry of 4:1. TPD shows there are no changes in film stoichiometry upon heating this film; however, compared to the spectra shown in Figure 6, it can be seen that there are changes in the infrared spectrum when the film is heated to 160 K. In particular, the absorption bands sharpen and shift in frequency. The apex of the band in the OH stretching region becomes more pronounced, and the entire band is more asymmetric with the development of a definite low-frequency shoulder near 3050 cm⁻¹. The band at 1750 cm⁻¹ becomes sharper and more distinct. The greatest change in the spectrum is seen in the bands between 1000 and 1500 cm⁻¹. Three bands emerge in this region upon heating to 160 K with frequencies of 1050, 1150, and 1267 cm⁻¹. The spectral changes observed in the 4:1 film upon, namely the sharpening of all the bands in the spectrum, is consistent with a film undergoing a transition from amorphous to a crystalline phase.

Temperature-dependent RAIR spectra were also recorded for films of H₂O:HBr stoichiometries <3:1. For these films, the TPD data (Figures 2 and 3) show that the composition of the film changes with temperature due to the loss of HBr. The

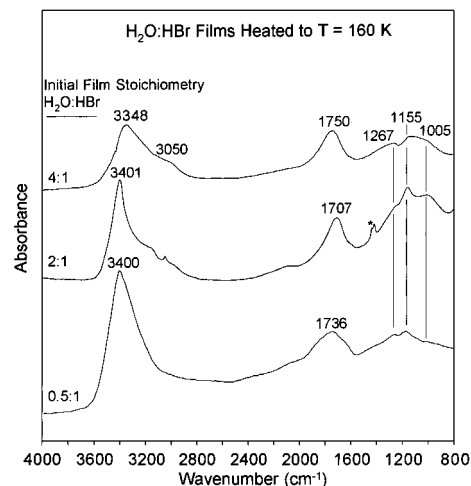


Figure 7. RAIR spectra of a H₂O:HBr film of 0.5:1, 2:1, and 4:1 stoichiometry heated to 160 K. Changes in the spectra are a result of an amorphous to crystalline transition of the 4:1 film and a combination of a composition and phase transformation for the 2:1 and 0.5:1 films. (The asterisk marks an impurity peak in one of the spectra.)

analysis of the TPD data in terms of film stoichiometry is shown in Figure 4. For the film of a 2:1 initial stoichiometry, TPD data indicate that the film changes to a 3:1 stoichiometry upon heating to 160 K. There are similar changes upon heating for films of H₂O:HBr stoichiometry near 2:1 to that of the 4:1 film; i.e., the apex of the OH stretching band sharpens while the entire band becomes more asymmetric with a more definite low-frequency shoulder. The band due to the H₃O⁺ bending mode becomes sharper, and there are now three distinct bands in the 1000–1500 cm⁻¹ region. These similar changes between a film that does not change composition to a film that does suggest that there is an amorphous to crystalline transition is occurring as well as a change in stoichiometry.

For films of H₂O:HBr stoichiometry <1:1, the 2591 cm⁻¹ band disappears upon heating to ~135 K (data not shown); this is consistent with the desorption of molecular HBr from the film. Heating the film to higher temperatures (160 K) causes some spectral changes, but these are not as distinct and clear as the other films examined, suggesting that the film may not have completely undergone an amorphous to crystalline transition. As the TPD indicate, there is a change in film stoichiometry to ~1:1. Assignments of the RAIRS spectra for these crystalline films (or nearly crystalline films) are summarized in Table 2.

Discussion

Comparison and Analysis of H₂O:HBr Thin Film Infrared Spectra. The RAIR spectra of the adsorption of HBr in ice at

140 K and the deposition of H₂O:HBr premade gas mixtures at 100 K clearly differ in both a qualitative and quantitative way from the lower temperature infrared spectra previously published^{20,21} as well as the lower temperature spectra measured here. One of the most significant differences is the broad band present between 2553 and 2590 cm⁻¹ associated with the presence of intact HBr in the film. This peak has been assigned as a combination of species including molecular HBr hydrogen bonded to water,^{20,21} as well as to a HBr ion hydrogen bonded to H₃O⁺.²¹ In our RAIR spectra recorded at higher temperatures, this band is present only for films that are in excess of HBr, i.e., for H₂O:HBr with stoichiometries of <1:1. This band observed near 2590 cm⁻¹ is most likely due to molecular HBr trapped in the film, and upon warming to 140 K this band decreases in intensity due to the desorption of HBr from the film.

An alternative explanation for the fact that the band near 2590 cm⁻¹ is not seen in the RAIR spectra is if all of the HBr molecules in the film were oriented parallel to the metal substrate. In this case, the band would be inactive according to the metal surface selection rule which states that only modes with a component perpendicular to the metal surface would be observed in RAIRS.²⁵ This explanation is not favored as it does not appear to be any reason why HBr would adopt a preferred orientation in these amorphous film.

Further heating of films deposited at lower temperature (<100 K) versus those deposited at higher temperatures (>100 K) also appears to be qualitatively and quantitatively different. The origin of these differences is unclear. However, it appears that the resulting films that form and their infrared spectra are strongly dependent on sample preparation, most notably deposition temperature. For example, there are even some differences in a HBr amorphous film of 4:1 stoichiometry deposited at 100 K compared to a 4:1 film formed from the adsorption of HBr into the ice film at 140 K. (There is a more pronounced shoulder near 1641 cm⁻¹ in the films deposited at 100 K compared to the HBr adsorption films prepared at 140 K.)

The assignment of the vibrational bands of the amorphous H₂O:HBr films with stoichiometries varying from <1:1 to ~4:1 are given in Table 2. In the current study, we have combined infrared data with mass spectral calibration to aid in the interpretation of the infrared spectra. This method of data analysis has been previously done in identifying dihydrate and trihydrate nitric acid thin films.²⁶ The assignments presented in Table 2 are based on literature assignments for hydronium ion, some earlier assignments of H₂O:HBr films,^{20,21} and some recent calculations for ions including H₅O₃⁺, H₇O₅⁺, and H₉O₄⁺.²⁷ The greatest uncertainty in these assignments is for the bands in the region between 1000 and 1500 cm⁻¹.

Finally, it should be noted that there is no evidence in the data presented here for the presence of a molecular state of HBr adsorbed on the surface of the film as has been seen by Graham and Roberts in their studies of HCl adsorption on ice.¹⁰ In their studies, ultrathin films on the order of 10 Å were used, whereas the films deposited here were nearly a factor of 10 larger; thus, the signal for a lower temperature HBr peak may have been difficult to detect. In addition, lower adsorption temperatures were used in their studies. Such conditions may favor the formation of a molecular adsorption state of the hydrogen halide.

Stoichiometry and Film Structural Changes upon Heating H₂O:HBr Amorphous Films to 160 K. It has been shown here from the TPD data that there is no significant change in stoichiometry for H₂O:HBr films of stoichiometry ≥3:1 upon heating. Therefore, any changes in the RAIR spectra for films

without change in stoichiometry are due to those associated with changes in the structure of the film. These changes are observed between 140 and 160 K, the same temperature range that amorphous to crystalline transition of pure ice films occurs.^{23,24} The sharpening of the absorption bands in the spectra indicates an amorphous to crystalline transition is taking place in the H₂O:HBr films as well.

For films of H₂O:HBr stoichiometries <3:1, there also appears to be a sharpening of the infrared spectral features upon heating to 160 K, consistent with an amorphous to crystalline transition. In addition, as seen from the TPD data, there is a concurrent change in film stoichiometry of one stoichiometric unit; e.g., films of initial stoichiometry of 2:1 are converted to a stoichiometry of 3:1. Importantly, the analysis of the TPD data specifically indicates that H₂O:HBr films formed under these conditions and heated at the rate of 1.5 K/s do not progress sequentially from amorphous to crystalline and then through several defined stoichiometries from 1:1 until 4:1 as has been previously suggested.^{20,21}

Finally, the data presented here are consistent with the recent phase diagram constructed by Chu and Chu for H₂O/HBr ice films. At the low temperatures used in this study a stable film of 4:1 stoichiometry is predicted, whereas films rich in HBr are not stable and lose HBr upon heating.

Conclusions

Here we have attempted to provide a more complete analysis of changes in the infrared spectra of H₂O:HBr films due to changes in film stoichiometry and film structure. This was accomplished by combining RAIRS and mass-calibrated TPD, which gave information initial stoichiometries and about changes in film stoichiometry upon heating. In addition, the higher temperatures used in this study, >100 K, reduced the amount of molecular HBr trapped in the film. The temperatures used here are closer to those in the stratosphere and upper troposphere, and therefore the spectra shown here may be more relevant to studies concerning the role of heterogeneous reactions of HBr in ice-containing aerosol.

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