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Heterogeneous Processing of Bromine Compounds by Atmospheric Aerosols: Relation to the Ozone Budget

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The depletion of ozone, particularly above Antarctica, has been investigated extensively to formulate public policy on the use of halocarbons. While it has been shown that heterogeneous reactions of chlorine compounds on stratospheric particulates cause the ozone hole, little is known of the analogous bromine mechanisms, even though it has been recognized for two decades that catalytic destruction of ozone by bromine could be more efficient than chlorine. Furthermore, field measurements and modeling calculations suggest that these heterogeneous (gas/surface) reactions are not restricted to the Antarctic regions but occur globally. We have performed laboratory measurements of the uptake of bromine compounds and other halogens on simulated stratospheric aerosols to help elucidate their role in catalytic ozone destruction cycles. Our studies contribute to the data base required to make assessments of the effects of human activities on global change, including the Montreal Protocol.

Background and Research Objectives

The dramatic changes in atmospheric chemical composition induced by heterogeneous (gas/surface) reactions on aerosol particulate have received considerable scientific scrutiny and international publicity recently, mainly in the context of the observed annual depletion of polar stratospheric ozone, popularly known as the "ozone hole". The role of chlorine-based heterogeneous chemistry on acidic ice clouds associated with this depletion has been irrefutably demonstrated qualitatively, and quantitative modeling of these processes has begun to show agreement with observations [1, 2]. In addition, gas/surface reactions on sulfate aerosols exacerbate chlorine induced ozone losses globally.

Despite the progress made in understanding these chlorine dominated processes, little is known of the analogous bromine mechanisms, even though it has been recognized for 20 years that catalytic destruction of ozone by bromine could be more efficient than

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*Principal Investigator, e-mail: jeanne.robinson@lanl.gov chlorine [3]. The calculated Ozone Depletion Potentials (ODP) are on average 50 times greater for brominated compounds than for the chlorinated standard reference CFC-11 [4]. The predominance of chlorine chemistry in polar heterogeneous mechanisms is a reflection of absolute concentration, with the measured tropical stratospheric influx of chlorinated species approximately 120 times greater than bromine species [5]. Nevertheless, bromine based heterogeneous chemistry is estimated to account for 25-50% of Antarctic polar ozone depletion [4].

Chlorine and bromine heterogeneous processes, which ultimately generate BrO and ClO, are synergistically coupled [6] through the gas phase catalytic cycle

$$\begin{aligned} &BrO + ClO \rightarrow Br + Cl + O_2 \\ &Br + O_3 \rightarrow BrO + O_2 \\ &Cl + O_3 \rightarrow ClO + O_2 \end{aligned} \qquad (1)$$

with a net ozone destruction of $2O_3 \rightarrow 3O_2$. This coupling mechanism elevates the importance of bromine chemistry when absolute concentrations of ClO drop below 1 ppb [4]. Consequently, leading atmospheric modelers recently called for the placement of increased international controls on chlorinated *and* brominated compounds beyond those currently enforced through the Montreal Protocol on Substances That Deplete the Ozone Layer [7].

Other catalytic cycles couple bromine with odd-hydrogen (BrO-HOx):

$$\begin{aligned} &BrO + HO_2 \rightarrow HOBr + O_2 \\ &HOBr + h\nu \rightarrow Br + OH \\ &Br + O_3 \rightarrow BrO + O_2 \\ &OH + O_3 \rightarrow HO_2 + O_2 \\ &\text{-------------------------------} \\ &2O_3 \rightarrow 3O_2 \end{aligned} \qquad (2)$$

and with itself (BrO-BrO):

$$\begin{aligned} &BrO + BrO \rightarrow 2Br + O_2 \\ &Br + O_3 \rightarrow BrO + O_2 \\ &Br + O_3 \rightarrow BrO + O_2 \\ &\text{---------------------------------} \end{aligned} \qquad (3)$$

$$2O_3 \rightarrow 3O_2$$

In these three cycles, the rate of the first reaction in each set involving BrO is controlling. Stratospheric measurements in the polar vortex during the rapid ozone loss episodes demonstrate that the BrO-ClO catalytic cycle is reponsible for 25-50% of the ozone loss above Antarctica with larger contributions above the Arctic [8]. Ozone loss from the BrO-HO_2 cycle is important in the extra-polar stratosphere [9], while the BrO-BrO and BrO-HO_2 cycles are believed to be the dominant chemical loss term for the observed Arctic marine boundary layer ozone loss [10]. Clearly processes controlling BrO levels are central to the global ozone budget.

A concerted international effort involving universities and government agencies from six North American and European countries bordering the Arctic was initiated in the early 1980's to investigate the phenomenon of Arctic Haze [11,12]. This effort, known collectively as the Arctic Gas and Aerosol Sampling Program, AGASP I and II, was designed to address the atmospheric and environmental effects of the tropospheric aerosol layer that permeates the Arctic and is believed to arise largely due to anthropogenic introduction of black carbon soot and sulfur dioxide into the Arctic basin from central Asia. Among the findings of this program was a pronounced inverse correlation between ozone levels in the lower Arctic atmosphere and filterable bromine during the polar Spring [13]. Several mechanisms that involve heterogeneous processing on Arctic aerosols have been proposed to account for this observation [14-17]. For example, incorporation of bromine from airborne seawater onto ice pack surfaces, and subsequent release as Br_2 at polar sunrise, has been proposed as the first step in a series of chemical reactions that result in ozone depletion in the Arctic boundary layer [13]. Other heterogeneous atmospheric chemical reactions are thought to participate in this process as well. Fan and Jacob [15] proposed a mechanism based on reactions known in aqueous phase chemistry, in which saline ice aerosols convert HBr, HOBr, and $BrONO_2$ rapidly back to radicals that participate in catalytic ozone destruction cycles.

A decade of stratospheric research has established that heterogeneous reactions on polar stratospheric clouds or aerosols surfaces that convert stable reservoir species ($ClONO_2$ and HCl) to active chlorine are essential to model the Antarctic ozone hole [9] as well as the global ozone loss trends documented by satellite observations [18,19]. Numerous laboratory studies of reactions on a variety of surfaces indicate that chlorine activation can be efficient [20]. Recently we developed a model based on the Eley Rideal mechanism where a gas-phase species reacts with a surface species (adsorbed H_2O) to describe the relative humidity dependence of the hydrolysis of $ClONO_2$ [21].

However, understanding of the analogous heterogeneous reactions involving bromine is more limited:

$$N_2O_5 + HBr(s) \rightarrow BrNO_2 + HNO_3(s) \qquad (4)$$

$$BrONO_2 + HBr(s) \rightarrow Br_2 + HNO_3(s) \qquad (5)$$

$$BrONO_2 + H_2O(s) \rightarrow HOBr + HNO_3(s) \qquad (6)$$

The photolysis of the product bromine species leads to BrO formation, one of the crucial gas phase catalysts in ozone depletion (Cycles 1-3). This lack of information regarding the heterogeneous reaction rates and mechanisms of bromine species is a glaring deficiency that we have sought to address in this work. Here we summarize the published literature for heterogeneous reactions of brominated compounds.

At the start of this project, the JPL publication *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, a compilation of kinetic data for modeling stratospheric chemistry [22], contained only one heterogeneous reaction involving bromine, N_2O_5 on NaBr, and that was a lower limit of reactivity measured at room temperature. Two measurements have since been conducted for HBr on ice [23, 24]. The bromine activation reaction:

$$HOBr + HBr(s) \rightarrow Br_2 + H_2O(s) \qquad (7)$$

on ice has recently been measured to be rapid enough to make it a viable mechanism to explain ozone losses in the Arctic marine boundary layer [25]. The hydrolysis reaction (6) has also been found to be fast on ice and sulfate aerosol surfaces [26]. It increases lower stratospheric odd-hydrogen, especially during sunrise and sunset, in agreement with field data and exacerbates ozone losses [27]. Measurements show that the trends of hydrolysis reaction probabilities on sulfate aerosols: $BrONO_2$ (0.8) >> N_2O_5 (0.1) >> $ClONO_2$ ($<10^{-3}$), are very different than those on ice: $BrONO_2$(0.3)~$ClONO_2$(0.3)>> N_2O_5 (0.01). Clearly fundamental reaction mechanisms have to be elucidated to resolve these differences. Comparative studies of heterogeneous reactions involving adsorbed HCl or HBr promise a potential for mechanistic insight. The current thinking is that both HBr and HCl have a strong affinity for ice and bind strongly to its surface by ionizing. The evidence for this is the absence of the molecular vibrational bands in molecular beam grazing incidence FTIR studies of ice films exposed to HCl and HBr at low temperatures (80-130K) [1]. However, these experiments have low sensitivity and are performed under conditions far from equilibrium or those encountered in the stratosphere. Our uptake measurements of both HBr and HCl on ice described herein show that the coverage of these species is 10 to

100 fold lower than commonly accepted. In addition while the solid hexahydrate phase of HCl is well characterized, only suggestive information is available for those for HBr [29]. In fact the phase diagram for HBr has not been updated since 1931 [30].

The objective of this research is to obtain thermodynamic and kinetic data relevant to the assessment of heterogeneous processing of brominated and other halogenated compounds on aerosol surfaces in the mid-latitude and polar stratosphere and the tropospheric Arctic boundary layer. We have developed a laboratory for the measurement of heterogeneous atmospheric processes with unique capabilities for preparation, characterization, and measurement of the heterogeneous reactivity of model ice surfaces. We have obtained data characterizing the phase and composition of these surfaces under relevant environmental conditions that can be used by atmospheric modelers to predict atmospheric chemical budgets.

Importance to LANL's Science and Technology Base and National R&D Needs

Bromine catalysis contributes significantly to the observed ozone losses in the lower stratosphere globally [3,31] and the Arctic marine boundary layer [14,15,32] in early spring. Photolysis of organic bromine compounds (methyl bromide and halons) supplies active bromine to the stratosphere. In the lower stratosphere, for a fixed atmospheric organic halogen loading, a much larger fraction of organic bromine is catalytically active (BrO) relative to that for organic chlorine (e. g. ClO from chlorofluorocarbons) [33]. This coupled with the faster kinetics of reactions of BrO than ClO, make bromine compounds remarkably potent in ozone destruction relative to the more abundant chlorine compounds (~70 times on a per atom basis).

While the amended Montreal Protocol has restricted the production of organic chlorine compounds and halons, regulatory decisions on methyl bromide (currently half of total organic bromine), which has both natural and anthropogenic sources, are awaiting better knowledge of the relative contributions of these two sources. In the marine boundary layer, field measurements [10], model calculations [34], and laboratory studies [35] suggest that active bromine is produced by surface catalytic halogen reactions of gas phase HOBr with bromide and chloride ions in sea ice. However the chemistry here is much more complex that that in the stratosphere. Our lack of understanding of atmospheric bromine chemistry and budgets is a significant impediment in predicting the future course of ozone and developing a rational policy on the use of methyl bromide.

Our data on the heterogeneous reactivity of halogenated compounds as a function of temperature and pressure is expected to have significant impact on the scientific study of these atmospheric systems. The compilation of data by the World Meteorological Organization (WMO) is critical to the formation of international policies such as the U.N. Framework Convention on Climate Change and the Montreal Protocols. The data provided by this research contributes directly to these concerns by providing accurate measures of the relative importance of these brominated and chlorinated species to ozone depleting mechanisms in the stratosphere. For example, our work on HCl uptake on ices under stratospheric conditions described herein is expected to be included in the upcoming report "The Scientific Assessment of Ozone Depletion:1998" under the auspices of the WMO-UNEP.

This work will also contribute to LANL's participation in the new Global Change Initiative mandated by DOE Secretary Peña in response to the upcoming Kyoto summit. Since greenhouse gases like CO_2 cool the stratosphere, increasing the occurrence of aerosols and clouds, it is imperative to understand heterogeneous reactions, such as those involving bromine and chlorine studied here, to develop public policy on energy related effluents like CO_2.

Scientific Approach and Accomplishments

The apparatus for the formation of the ice and supercooled liquid samples is centered around a chamber capable of 10^{-7} torr vacuum, shown in Figure 1. A cold support is suspended in the chamber and is temperature controllable in the 85K to 320K regime. Water vapor is introduced into the chamber from a liquid reservoir and condensed at selected pressures and temperatures. Typically we grow amorphous ices at about 85 K and then anneal them to temperatures above the amorphous to crystalline transition to form polycrystalline ice films at stratospheric temperatures. The surface area of the simulated aerosols is measured by physical adsorption of inert gases in the same chamber. We can control the surface area of the ice film as well as the flow rate of adsorbates we introduce to the chamber. The chamber is also coupled to a quadrupole mass spectrometer for gas phase measurements which allow us to verify the equilibrium nature of the experiment and determine the vapor pressure of water, the adsorbate, and ultimately any reaction products. An FTIR is available for bulk aerosol characterization.

The surfaces of the simulated aerosols are probed by a laser technique known as second harmonic generation (SHG). The optical train is shown in Figure 1; quartz windows on the vacuum apparatus allow optical access for the laser and the SH signal. Second harmonic generation is a relatively simple optical measurement that offers the extremely valuable attribute of probing the surface properties of a system, as opposed to the bulk. At the solid/vapor or liquid/vapor interface, a small fraction of the incident laser at frequency ω is converted to light at the second harmonic frequency (2ω) with an efficiency that depends on the chemical composition and degree of ordering at the interface [36]. Thus, the SHG signal is sensitive to the *surface* composition and thermodynamic phase of the aerosols. Because the surface reactivity is of interest in heterogeneous atmospheric chemistry, this approach is preferable to more common techniques, such as FTIR, which probe only bulk composition.

The laser system we use is a pulsed, picosecond Nd:YAG laser providing 532 nm light at 10 Hz. The 266nm second harmonic signal generated in reflection from the sample is detected by a solar blind PMT following wavelength selection by color filters and a 0.25m monochromator. We have demonstrated the sensitivity of SHG to adsorbed acids and organics on ice films [37]. The SHG signals we observe from adsorbate doped ices are several orders of magnitude larger than that for neat water ices. In addition, we can distinguish different thermodynamic phases (e.g. nitric acid trihydrate or NAT vs. nitric acid monohydrate or NAM) [38] as well as different acidic aerosols (e.g. HCl vs. HNO_3 vs. H_2SO_4) from their respective temperature dependent SH responses.

The vapor pressures of water and the adsorbate over the ice film are monitored using a quadrupole mass spectrometer (Pfeiffer-Balzers QMG 421-3) coupled to the vacuum chamber through a gas dosing valve. The total background pressure of the mass spectrometer is $<10^{-10}$ Torr. The inlet is a quartz lined, heated capillary. The mass analyzer is configured 90° off axis, with the ion source perpendicular to the SEM detector. The water vapor pressure was monitored at m/z=18 during the annealing and subsequent cooling of ice films condensed at 85 K. The water ion signal was converted to pressure using a 1 Torr capacitance manometer at high pressures and the recent compilation of vapor pressure data for water over ice I_h in the 170 to 250 K temperature range reported by Marti and Mauersberger [39]. The sensitivity is about 10^{-6} Torr water.

Our measurements are aimed at characterizing the uptake and surface composition of model atmospheric aerosols, such as nitric acid/water ice and HBr or HCl doped water ice. We have demonstrated the ability to use SHG measurements as a function of temperature and pressure to determine the surface thermodynamic phase of nitric acid doped ice films [38]. These measurements depend on the sensitivity of SHG to surface structure. We have used this approach to characterize the model aerosols with respect to crystallization, melting transitions, composition, and stable thermodynamic phase. In addition, we have shown that SHG is a quantitative probe of the adsorption of gases on heterogeneous substrates, such as water ice [37]. We developed a formalism, which relates classical physical adsorption theories such as Brunnauer-Emmett-Teller theory to the SHG response [37]. This approach allows us to quantify the coverage under conditions, which preclude ultra-high vacuum techniques. In addition, we are able to directly measure the relative interaction energies between the adsorbate-adsorbate and the adsorbate-substrate.

We have studied HBr interactions with porous polycrystalline ice under near stratospheric conditions [40]. We monitor the transformations at the ice surface as a function of HBr exposure or temperature using SHG. The upper panel in Figure 2 shows the SH response we observed for an ice doped with 0.7 monolayers HBr during annealing from about 90K past the melting point of about 200K. Signatures in the SHG signal suggest formation of two different phases prior to melting. The lower panel shows the adsorption isotherm for HBr on water ice using SHG detection. The SHG response is small initially and increases after a hydrate phase is formed. The low SHG intensity suggests that a liquid or liquid-like metastable phase of HBr exists, which then nucleates to a hydrate.

We have seen similar behavior for HCl adsorption on water ice. Using the mass spectrometer we have also measured the vapor pressures of HBr and H_2O over ice at lower coverages of Hbr. Figure 3 shows the vapor pressure of HBr measured during the slow introduction of the adsorbate onto a polycrystalline water ice film. Pure water ice was exposed to a extremely small steady flow of gaseous HBr (1×10^{-8} moles sec^{-1})) to ensure equilibrium. The time-integral of the gaseous HBr flow normalized by the ice surface area (~$6 m^2$) in molecules/cm^2 is shown in the horizontal axis. The equilibrium vapor pressure of HBr in torr above ice measured by calibrated quadrupolar mass spectrometer signals at 79 amu (^{79}Br) and 80 amu ($H^{80}Br$), is shown on the vertical axis. The HBr pressure rises sharply when the ice has been coated with a monolayer of HBr (2×10^{14} molecules cm^{-2}) and the hydrate phase is nucleated. These vapor pressure measurements (Figure 2) are modeled by classic physical adsorption theory. An analysis of the HBr isotherm using Langmuir-Bragg-Williams formalism [41] yields an adsorption energy of -7.7 kcal/mole.

Figure 4 shows the uptake of HCl on water ice [42]. At temperatures below 200K and HCl pressures from 10^{-7}torr to 3×10^{-6}torr, as monitored with a quadrupole mass spectrometer, we observe adsorption from submonolayer coverages up to one monolayer of HCl. Saturation of this monolayer is seen as a dramatic rise in HCl pressure at a coverage of 2×10^{14}molecules/cm^2. At that point, a phase transition to the hydrate is observed, with an apparent nucleation barrier of $P_{HCl} \sim 1 \times 10^{-4}$ torr. At 200K or higher, the hydrate does not nucleate. Both the hydrate and the adsorbed monolayer phase melt to the liquid when heated above 200K. Concurrent surface second harmonic generation measurements corroborate these phase transitions. The adsorption isotherms for HCl coverages below $2x10^{14}$molecules/cm^2 are modeled with Langmuir-Bragg-Williams theory [41] that includes a constant adsorption energy and lateral adsorbate interactions. The picture that emerges from this work is one in which HCl adsorption is very small under stratospheric conditions, i.e. <0.1 monolayer for $1x10^{-7}$torr HCl vapor pressure at 180-190K.

Results on HBr/ice can be compared with those on HCl/ice to gain insight into heterogeneous halogen activation mechanisms and their impact on atmospheric chemistry. Both data sets show that the coverage of HBr or HCl is very small at stratospheric pressures (extrapolating to about 10^{-9} Torr and 10^{-7} Torr, respectively). HBr uptake on ice has also been measured in a flow-tube, albeit without surface area measurements [24]. They deduce HBr coverage on PSCs of 0.1% under stratospheric conditions. In this work, we have measured similar low coverage for both HBr and HCl on ice in a systematic way [40, 42]. These mechanistic findings are in disagreement with the high heterogeneous reaction probabilities used in atmospheric models, and warrant a detailed examination. Atmospheric models typically use coverages that are much higher, approaching monolayer coverage. Our data suggest that such models severely overestimate the importance of heterogeneous reactions that involve adsorbed HBr or HCl.

We have monitored the vapor pressure of the brominated agricultural fumigant, CH_3Br, over a pure H_2O ice substrate at low temperature. Our results suggest that the CH_3Br/water ice system is reactive; hydrocarbons and HBr were detected by mass spectrometry while vapor pressure measurements, and melting point determinations provided further corroboration. The reaction may be photoinitiated by the laser pulse. In a preliminary measurement of a different heterogeneous reaction, we identified the HNO_3 surface product from the hydrolysis of N_2O_5 on water ice by observation of SHG and a melting point determination.

We have also used SHG to monitor the evolution of a simulated Type I NAT Polar Stratospheric Cloud particle to a Type II particle by water condensation (Figure 5) [38]. The extent and speed of diffusion of the H_2O adsorbate into the nitric acid substrate is interesting with respect to the hydration reactions. Our observed adsorption spectra for this system, and many other acid/water ice and organic/water ice systems, indicate significant migration of species into our porous, laboratory grown ices [37]. These results are of considerable importance with respect to modeling the kinetics of surface mediated process on laboratory ice substrates. It is clear that reaction is not limited to the small geometric surface of the ice films, but that the significant area represented by the highly porous interior must be considered [43].

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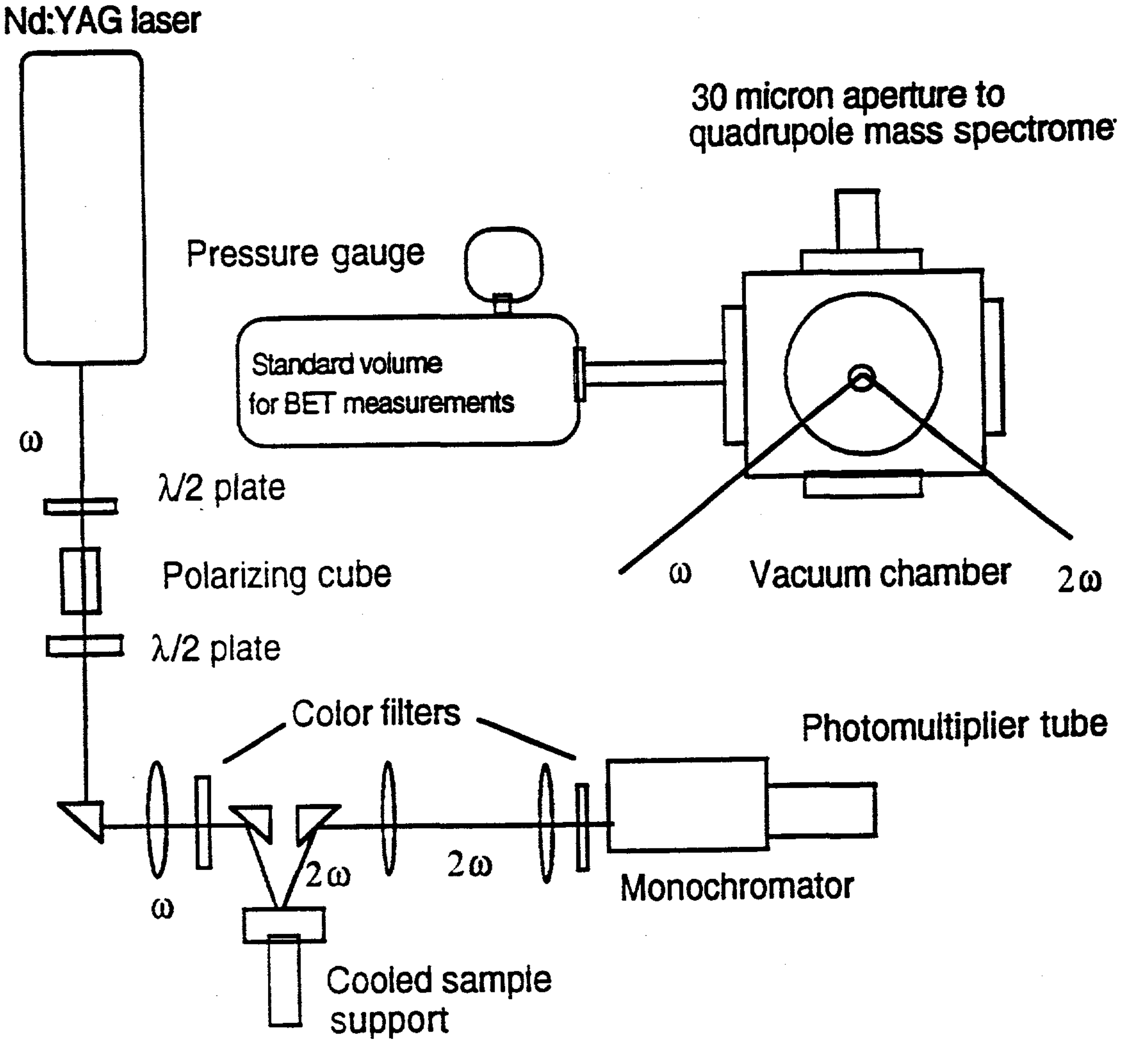
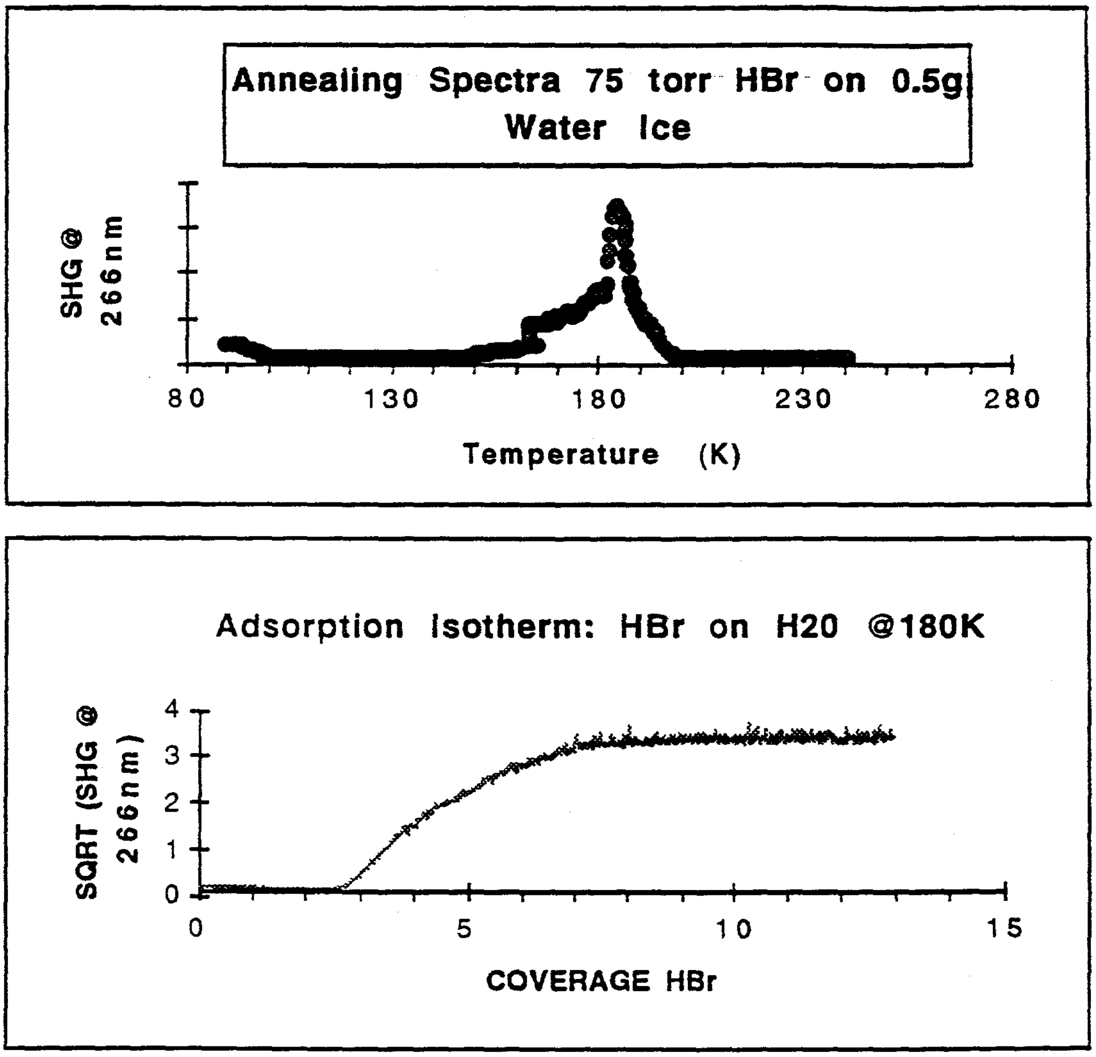


Figure 1. Schematic diagram of the sample vacuum chamber and the optical train associated with the second harmonic generation measurement. The calibrated tank is used for measurement of surface area by physical adsorption. Gas phase concentrations are measured via quadrupole mass spectrometry.


Annealing Spectra 75 torr HBr on 0.5g Water Ice

Adsorption Isotherm: HBr on H20 @180K

Figure 2. SHG Spectra for HBr/ice. The upper panel shows the SHG intensity as a function of temperature for a porous water ice with 0.7 monolayers HBr adsorbed. The lower panel showns an SHG adsorption isotherm for HBr at 180K.

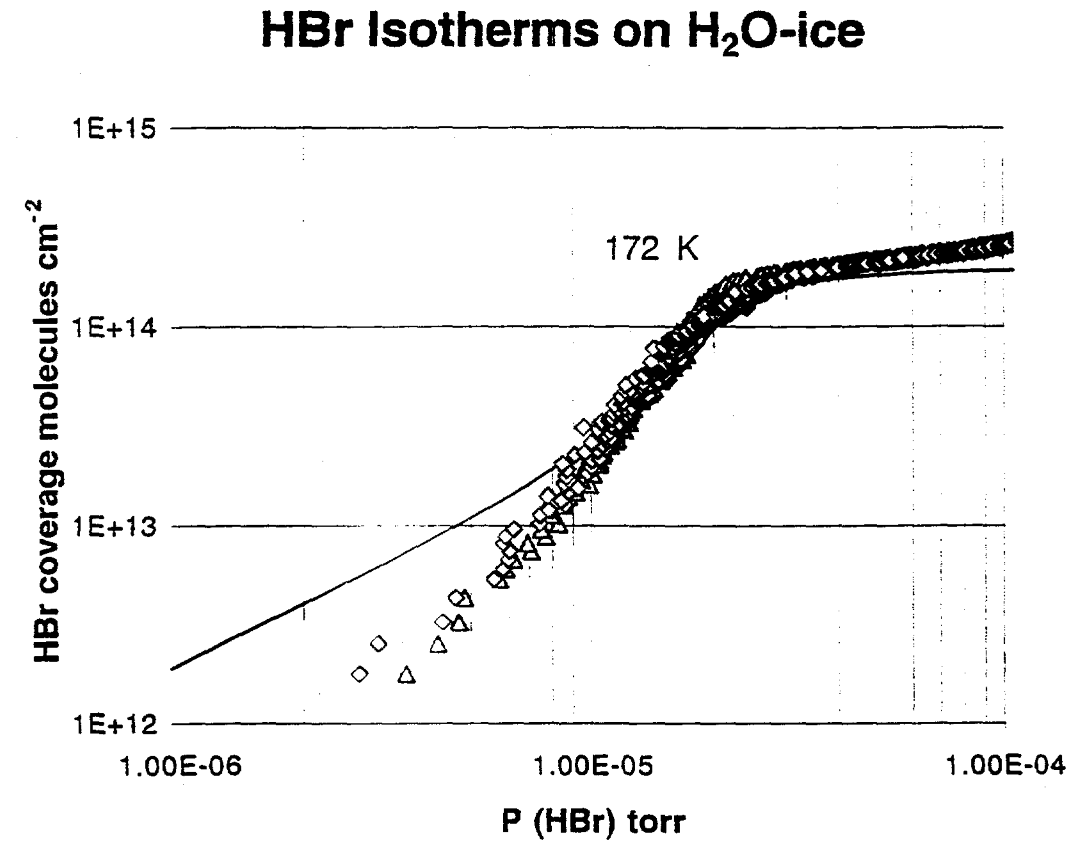


Figure 3. Pressure adsorption isotherm of HBr on ice measured using quadrupole mass spectrometry.

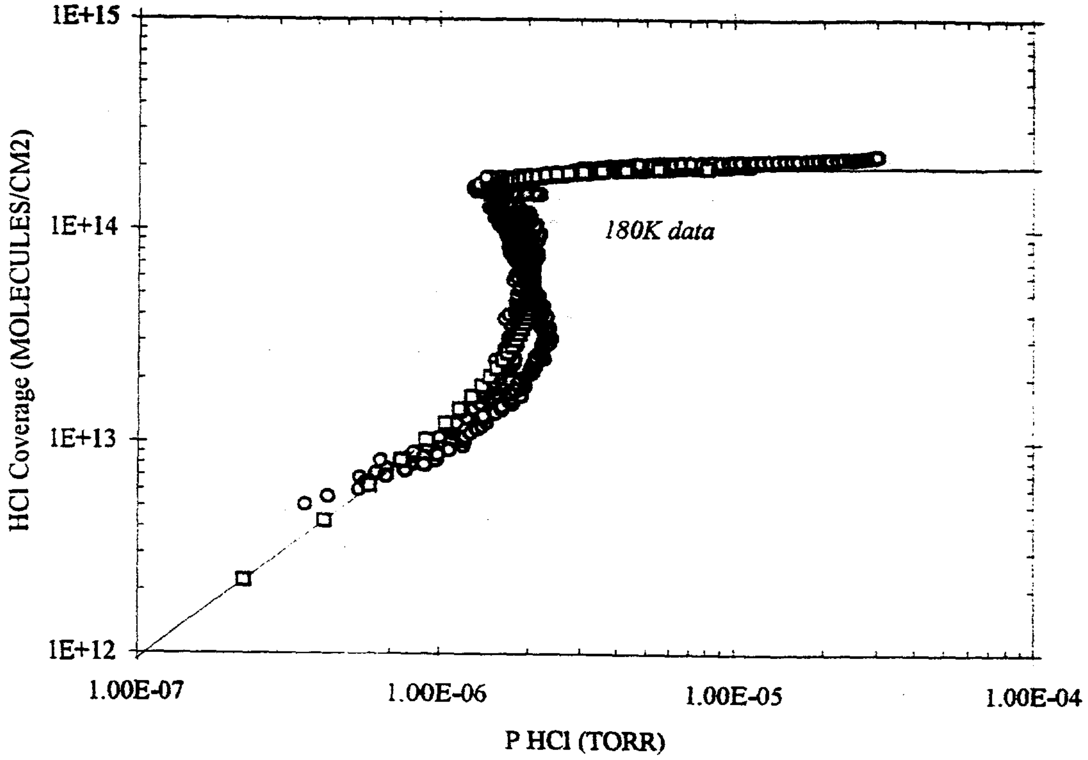


Figure 4. Pressure adsorption isotherm of HCl on ice measured using quadrupole mass spectrometry.

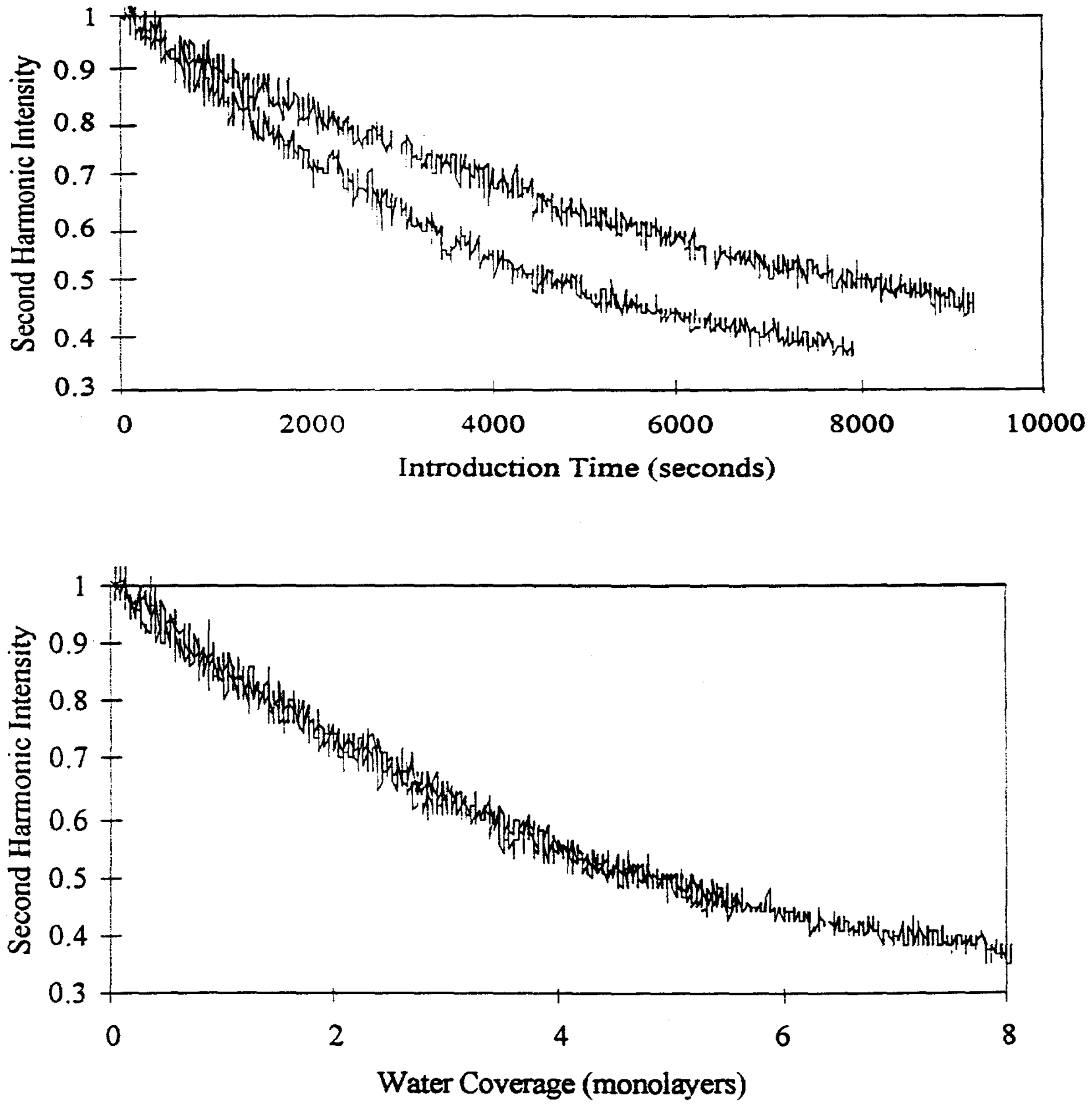


Figure 5. H_2O adsorption into a porous, nitric acid hydrate substrate. The upper panel shows the SH intensity as a function of introduction time onto two substrates of different area at 85K. When the spectra are normalized to substrate area, in the bottom panel, the identical signal dependence on adsorbate coverage is apparent.