A surface chemistry model for nonreactive trace gas adsorption on ice: Implications for nitric acid scavenging by cirrus

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Abstract. According to recent measurements HNO₃ nearly saturates laboratory ice films in flow tubes for vapor pressures above 10⁻⁷ torr and temperatures below 230 K. In the upper troposphere the HNO₃ vapor pressure is in the range of 1 to 3 x 10⁻⁴ torr and therefore the current laboratory estimates of saturation may not hold in the atmosphere. Here, with the aid of a surface chemistry model and laboratory data we estimate that the binding energy for HNO₃ adsorbed on ice is about -14.2 ± 0.2 kcal mol⁻¹. Using the surface model, we explore the sensitivity of HNO₃ scavenging efficiency to cirrus cloud temperature, ice number density, and HCl competitive adsorption.

Introduction

Ozone production in the upper troposphere is catalyzed primarily by nitrogen oxides [Singh et al., 1996; Jacob et al., 1996]. Since ozone is an effective greenhouse gas in the upper troposphere [Lacis, 1990], it is important to understand the distribution of nitrogen between nitrogen oxides and their main reservoir species, HNO₃. Overall, global transport-chemistry models overestimate the abundance of gas phase HNO₃ in the upper troposphere compared to observations [Thakur et al., 1999], particularly during spring and summer [Tabazadeh et al., 1998]. It has been suggested that cirrus clouds provide an important global sink for HNO₃ in the upper troposphere [Lawrence and Crutzen, 1998]. Here, by using a surface chemistry model, we investigate under what set of conditions and assumptions cirrus can be considered as an important potential scavenger of HNO₃ in the upper troposphere.

Surface Chemistry Model Description

The Langmuir surface chemistry model used here is described in detail by Tabazadeh and Turco [1993] with one major modification. In the analysis described here we assume a dissociated rather than a molecular state for HNO₃ and/or HCl adsorbed on ice in agreement with laboratory studies, indicating that both HCl and HNO₃ ionize on ice surfaces [Abbatt et al., 1992; Zondlo et al., 1997]. For clarity of presentation the preexponential factors for the adsorption and desorption rate constants are simplified compared to the relations given in Tabazadeh and Turco [1993].

The rate of gas adsorption onto a solid surface for a mobile film is given by [Laidler et al., 1940],

\[
k_a = \frac{C}{\sqrt{MT}} \exp\left[-\frac{e_1}{RT}\right]
\]

(1)

where \(C = 1.111 \times 10^6 \text{ (kg}^{-1} \text{K}^{-1/2} \text{torr}^{-1/2} \text{sec}^{-1})\), \(M\) is molecular weight of the adsorbing gas in kg, \(T\) is temperature in K, \(R\) is the gas constant, and \(e_1\) is the energy of activation for adsorption per single molecule.

The rate of gas desorption is given by [Laidler et al., 1940],

\[
k_d = 10^{13} \text{ (sec}^{-1}) \exp\left[-\frac{e_2}{RT}\right]
\]

(2)

where \(e_2\) represents the energy of activation for the desorption of a single molecule. The equilibrium adsorption constant \(K_{eq}\) is defined as

\[
K_{eq} = \frac{k_a}{k_d} = \frac{C}{10^{13} \text{ (sec}^{-1}) \sqrt{MT}} \exp\left[\frac{\Delta G_{ads}}{RT}\right]
\]

(3)

where \(\Delta G_{ads} = -(e_2 - e_1)\) is the free energy of adsorption per single molecule. Here we assume that \(\Delta G_{ads}\) is independent of temperature.

Assuming that HNO₃ dissociates on the ice surface, the adsorption process can be presented by the following chemical equation:

\[
\text{HA(gas)} \leftrightarrow \text{H}^+(\text{ad}) + \text{A}^-(\text{ad})
\]

(4)

In the case of a nonreactive dissociative gas, the Langmuir isotherm describes the interaction of the gas with the surface in terms of the equilibrium surface coverage (\(\theta\)), given by

\[
\theta = \frac{\alpha K_{eq}^{1/2} P_g^{1/2}}{1 + K_{eq}^{1/2} P_g^{1/2}}
\]

(5)

where \(P_g\) is the vapor pressure of the adsorbed gas over the surface in units of torr, and \(\alpha\) is the fraction of surface sites that are available for adsorption.

Overall for most surface chemistry studies the adsorbing material is nonvolatile (i.e., H₂O adsorption on the silicon surface). Thus all the surface sites are initially available for adsorption. However in the upper troposphere the most likely adsorbing surface is ice, which is volatile and therefore some of the surface sites on ice are occupied by H₂O molecules that continuously adsorb and desorb from the surface. Since the remaining vapor pressure of H₂O over ice greatly exceeds the mixing ratio of trace gas species, such as HNO₃ and HCl, a significant fraction of surface sites on ice are taken up by water and their effect on the adsorption process in the atmosphere must be accounted for.
Laboratory Data Interpretation and Analysis

Figure 1 illustrates the variation of HNO₃ coverage on ice as a function of vapor pressure for different assumptions of \( \Delta G_{ads} \) calculated using equations (1) through (6). Also plotted are raw laboratory adsorption data [Abbatt, 1997; Zondlo et al., 1997]. Using \( \Delta G_{ads} = -14.2 \pm 0.2 \text{ kcal mol}^{-1} \) in equations (1) through (5) yields a factor of about two change in the coverage in agreement with the laboratory data of Abbatt at 228 K over the vapor pressure range of 1.3 \( \times 10^{-7} \text{ torr} \) to 3.1 \( \times 10^{-6} \text{ torr} \) (see Figure 1). In addition, Abbatt data suggests that the HNO₃ coverage on ice at full saturation is near 2.7 \( \times 10^{14} \text{ molecules cm}^{-2} \) at 228 K, which is equivalent to about 27 % of the total number of sites (~ \( 10^{15} \text{ cm}^{-2} \)) available for adsorption on a typical surface [Adamson, 1989]. Assuming that the HNO₃ coverage on ice at full saturation is 27% at 228 K, the extrapolation of Abbatt's data to lower vapor pressures using the model yields a coverage of about 0.04 monolayer (~ \( 5 \times 10^{13} \text{ molecules cm}^{-2} \)) of HNO₃ on ice at \( 10^8 \text{ torr} \). Also plotted in Figure 1 is the data of Zondlo et al., which is consistent with an adsorption energy equal or greater than ~13.2 kcal mol\(^{-1}\) in magnitude. In Figure 2 the sensitivity of HNO₃ surface coverage to temperature is shown for different assumptions of the adsorption free energy. A factor of 4 change in the observed coverage is only consistent with an adsorption energy of ~14.2 \pm 0.2 kcal mol\(^{-1}\). Thus using an adsorption free energy of ~14.2 \pm 0.2 kcal mol\(^{-1}\) in the model reproduces well the observed trends [Abbatt, 1997] in both pressure and temperature.

Atmospheric Applications

In the previous section we emphasized the fact that in order to extrapolate HNO₃ laboratory coverages into atmospherically relevant values, the use of a surface adsorption model is required. In other words, it is incorrect to assume that since laboratory coverages are, for example, a significant fraction of a monolayer, then atmospheric coverages are also the same fraction of a monolayer irrespective of temperature and pressure dependencies. In addition, for computing atmospheric coverages, the surface adsorption model must be coupled to mass conservation relations for all the species adsorbed on the surface. To include the effect of HNO₃ depletion on the coverage, the following equations must be solved simultaneously:

\[
P_T = P_g + P_a
\]

\[
\theta = \frac{\alpha K_{eq}^{1/2} p_g^{1/2}}{1 + K_{eq}^{1/2} p_g^{1/2}}
\]

\[
\theta = \frac{\beta p_a}{S}
\]

Where \( P_T \) is the total HNO₃ partial pressure in torr, \( P_g \) is the atmospheric equilibrium HNO₃ vapor pressure over ice in torr, \( P_a \) is the HNO₃ concentration in the adsorbed state in torr, \( \beta \) (~ \( 9.656 \times 10^{13} \text{ T}^{-1} \)) is a conversion factor, \( \sigma \) (~\( 10^{15} \)) is the surface site density in cm\(^{-2}\), and \( S \) is the ice surface area density in cm\(^2\) cm\(^{-2}\). By iterating the above equations \( P_a \) can be...
evaluated as a function of $T_f$, temperature, and ice surface area density.

In addition, ice particle surfaces in the atmosphere may differ greatly from pristine surfaces generated in the laboratory. For instance, the adsorption of HCl (or other trace species) on ice may significantly reduce the HNO$_3$ coverage as a result of competitive adsorption. To account for HCl competition equation (6b) must be replaced by:

$$\theta = \frac{aK_{eq}^{1/2}p_{HCl}^{1/2}}{1 + K_{eq}^{1/2}p_{HCl}^{1/2} + K_{eq, HCl}^{1/2}p_{HCl}^{1/2}}$$

(7)

Adding the mass balance relations for HCl uptake on ice to the above set of equations (6a-6c), the effect of HCl in reducing the HNO$_3$ coverage can be evaluated. As shown in Figure 3, for a typical HNO$_3$/HCl mole ratio of 2 [Brasseur and Solomon, 1986], HCl can potentially reduce the HNO$_3$ coverage on cirrus by about 30% at ~210 K if the adsorption energy for HNO$_3$ and HCl binding on ice are equivalent. On the other hand, if the HCl adsorption energy on ice is larger than that of HNO$_3$, then the HNO$_3$ coverage on ice may be reduced by as much as a factor of 4 due to the HCl competitive adsorption (Figure 3).

In Figure 4 the fraction of HNO$_3$ removed on ice ($p_a / p_f$) is calculated as a function of temperature using equation (6). A typical global ice water content (IWC) for cirrus inferred from lidar and radar studies is about 25 mg m$^{-3}$ [Dowling and Radke, 1990; Mace et al., 1997]. The surface areas shown in Figure 4 are calculated by distributing 25 mg m$^{-3}$ of water over a monodispersed size distribution of ice crystals with different number densities, which are indicated on top of the chart. It is important to point out that our results shown in Figure 4 don’t take into account the effect of HNO$_3$ taken up in the bulk of ice particles. However, new laboratory data suggest that the HNO$_3$ bulk uptake is negligible and can be ignored [Sommerfeld et al., 1998].

As shown in Figure 4 near complete removal of HNO$_3$ on cirrus can occur in lee wave clouds, in agreement with in situ measurements [Weinheimer et al., 1998]. However, lee wave clouds in general have short lifetimes, and therefore the HNO$_3$ removal process is almost entirely reversible. On the other hand, we believe irreversible removal of HNO$_3$ will only occur on cirrus in which the average ice crystal radii exceeds 100 micron (labeled in Figure 4 as precipitating cirrus). Ice crystals less than a 100 micron are unlikely to survive a 1.5 km (a typical cirrus cloud thickness [Dowling and Radke, 1990]) fall to below a cirrus cloud base [Rogers and Yau, 1989], where the majority of ice particles are evaporating. We refer to this class of clouds (average radii < 100 micron) as background cirrus (see Figure 4), and speculate that HNO$_3$ will be released back to the gas phase within a few kilometers from the altitude, where it was originally adsorbed. Since cirrus clouds often form between 1 to 3 km below tropopause [Dowling and Radke, 1990; Mace et al., 1997], it is unlikely that multiple background cirrus formation in this altitude band would result in removing HNO$_3$ to altitudes 3 km below the tropopause. Therefore, the adsorption process by background cirrus should also be a large extent reversible.

For precipitating cirrus (streaks of ice particles often observed beyond the cirrus cloud base), less than 30% of gas phase HNO$_3$ may be irreversibly removed by cirrus per cloud
episode, depending on the cloud temperature and the ice number density. Although it is important to point out that the streaks of large ice particles are often observed in warm clouds (T > 230K) [e.g., Sassen et al., 1989], and therefore the scavenging efficiency by precipitating cirrus is further reduced to below 10% (see Figure 4) per cloud episode. For comparison in Figure 4 the fraction of HNO3 removed by cirrus based on the assumption (a constant 0.1 monolayer coverage of HNO3 on ice for all temperatures) used in the Lawrence and Crutzen [1998] study is also shown. It is clear that especially for a warm precipitating cirrus (T > 230 K), the assumption used by Lawrence and Crutzen will greatly overestimate the scavenging efficiency of HNO3 by cirrus.

To fully assess the extent of HNO3 removal by cirrus the scheme outlined here should be incorporated into a 3-D model, which is beyond the scope of this work. However by combining a few different types of datasets (aircraft and satellites) some qualitative information can be extracted on the effectiveness of cirrus to remove HNO3. For instance, aircraft HNO3 gas phase measurements in the upper troposphere over the Western Pacific (measurements taken during NASA PEM West A and B field programs) show a strong seasonal variation, with much higher concentrations measured during winter as compared to summer [Thakur et al., 1999; Tabazadeh et al., 1998]. Thus if cirrus was the main scavenger of HNO3 in the upper troposphere, then one would expect noticeably more cirrus cloud cover over this location in the summer relative to winter in order to explain the seasonal trend observed in the HNO3 data. On the contrary, SARG II cirrus cloud statistics over the Western Pacific show only small seasonal variations in cirrus with roughly 15% more cloud cover in winter as compared to summer [Wang et al., 1996]. Obviously the weak seasonal trend in the cirrus cloud cover seen by SARG II goes against the strong seasonal behavior observed in the HNO3 data over the Western Pacific. Hence it is unlikely for cirrus to have been strongly involved in removing HNO3 from the upper troposphere over this location. However, even though measurements over the Western Pacific (along with few other locations described in Thakur et al. [1999] showing the same seasonal trends in HNO3) are suggestive in illustrating a lack of positive correlation between cirrus and HNO3, they are not conclusive. In fact the seasonal variation seen in the HNO3 data may be partly related to different sources of NOx to the region during the two periods [Thakur et al., 1999]. Thus future aircraft and satellite data combined with 3-D modeling studies are needed to better quantify the global relationship, which may or may not exist between cirrus and HNO3.

Conclusions

In this paper we outlined a surface chemistry model for calculating HNO3 coverage on ice in the upper troposphere. Current global chemistry-transport calculations indicate that assuming a constant surface coverage of about 0.1 monolayer of HNO3 on ice could result in a significant depletion of gas phase HNO3 by cirrus [Lawrence and Crutzen, 1998]. However we have shown that HNO3 coverage on ice depends strongly on cirrus cloud temperature, HNO3 vapor pressure and ice number density. Therefore assuming a constant surface coverage for all atmospheric conditions is not appropriate. The lack of a seasonal correlation between HNO3 and cirrus over the Western Pacific may indicate that precipitating cirrus was not a key player in removing HNO3 from the upper troposphere over this location. Finally, to narrow down the range of uncertainty associated with the adsorption energy of HNO3 on ice, which is the key parameter for surface chemistry calculations, laboratory data for HNO3 adsorption on ice in the presence and absence of HCl and other possible competitive absorbers at low vapor pressures and temperatures are needed.

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References


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