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Modification of Heterogeneous Chemistry by Complex Substrate Morphology

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Abstract
This is the final report of a one-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). Chemistry in many environmental systems is determined at some stage by heterogeneous reaction with a surface. Typically the surface exists as a dispersion or matrix of particulate matter or pores, and a determination of the heterogeneous chemistry of the system must address the extent to which the complexity of the environmental surface affects the reaction rates. Reactions that are of current interest are the series of chlorine nitrate reactions important in polar ozone depletion. We have applied surface spectroscopic techniques developed at LANL to address the chemistry of chlorine nitrate reactions on porous nitric and sulfuric acid ice surfaces as a model study of the measurement of complex, heterogeneous reaction rates. The result of the study is an experimental determination of the surface coverage of one adsorbed reagent and a mechanism of reactivity based on the dependence of this coverage on temperature and vapor pressure. The resulting mechanism allows the first comprehensive modeling of chlorine nitrate reaction probability data from several laboratories.

Background and Research Objectives

Chemistry in many environmental systems is determined at some stage by heterogeneous reaction with a surface. Some examples include the reaction of urban pollutants with carbonaceous soots or aerosol fogs, reactivity and transport of contaminants in soils, the chemistry of combustion products on ash in industrial incineration, and most recently, the destruction of stratospheric ozone on cloud particulate. In all of these systems the strategy of understanding the heterogeneous chemistry involves simulating the surface in the laboratory and applying well-known techniques of surface chemistry applicable to flat surfaces, or gas phase chemistry to indirectly probe the destruction of reagents and formation of products. Typically, however, the relevant surface exists as a dispersion or matrix of particulate matter or pores, and the molecular surface is subject to severe perturbations as a result of the extreme macroscopic curvature induced by diameters on the order of 10Å to 1000Å. This is true of all the examples presented above. In addition, other mechanisms, such as
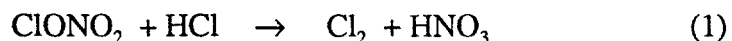

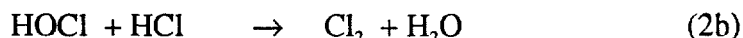[*] Principal Investigator, E-mail: henson@lanl.gov

the constraint of transport properties, reflected in increased collision frequencies with confining walls and the restriction of mixing in a porous sample also may affect the chemistry of the surface-reactant system. *A true determination of the heterogeneous chemistry of a particular system must therefore address the extent to which the complexity of the environmental surface affects reaction rates determined on an ideal, infinitely flat surface.*

The most severe perturbation induced by extreme curvature is through the surface chemical potential. Described by the Kelvin effect,[1] strong curvature induces significant changes in the thermodynamic properties of the interface, changing the equilibrium vapor pressure over a surface by as much as 70%. This dramatic change in stability can lead to changes in the surface concentration of an adsorbate, or the equilibrium thermodynamic phase of a substrate. These thermodynamic perturbations can strongly alter surface meditated chemistry. Two major mechanisms characterize reaction at a flat surface.[2] In the Langmuir-Hinshelwood (LH) mechanism, reaction occurs between two adsorbed molecules. The limiting rate as a function of concentration goes through a maximum and decreases to zero. In the Langmuir-Rideal (LR) mechanism, the reaction occurs between an adsorbed species upon collision with a gas phase reactant. The limiting concentration-dependent rate in the LR mechanism is nonzero. These two mechanisms thus display dramatically different limiting rates as a function of surface concentration. In addition, these simple limits are valid for desorbing products that do not interfere with reaction.

Adsorbed products will inhibit the rate in a way that is strongly affected by the mobility of the adsorbed phase, typically saturating for a stationary phase and linearly increasing for a mobile phase.[2] Modification of the kinetics of reaction on porous or particulate surfaces is thus possible either through the surface concentration or through the thermodynamic phase of a reagent or product. For molecular substrates, such as ice or glass phases, modification by the curvature can also proceed from the substrate itself. Extreme curvature must induce considerable surface heterogeneity due to the strain of projecting a rigid single crystal structure onto a curved topology. This heterogeneity may be expected to increase adsorption, given the strong interaction of adsorbed species with steps that is observed on metal and oxide surfaces.

Coupled reactions that are of considerable current interest and are susceptible to the type of modification discussed above include the series of chlorine nitrate reactions important in polar ozone depletion:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (1)$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \qquad (2a)$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (2b)$$

These reactions proceed on particulate ice in the stratosphere and serve to activate the Cl_2 as a gas phase product, which subsequently attacks ozone. The history of the study of these reactions affords a lesson in the changing paradigm of investigations in heterogeneous chemistry in environmental systems.

The experimental investigation of these heterogeneous reactions and their impact on ozone depletion has developed in fairly well-defined stages. Initially the challenge was adequately simulating the low partial pressures and temperatures characteristic of the stratosphere. A considerable body of data characterizing the overall reaction rates under relevant conditions was quickly obtained and refined by measurements of the disappearance of reagent and appearance of products in the gas phase.[3] As substrate ices reflecting the complexity of the stratospheric environment were addressed experimentally, it became apparent that simple rates obtained over a few surfaces would be inadequate to provide realistic predictive power in the complex environment of the stratosphere. For instance the rates of reactions 1 and 2a exhibit a dramatic dependence on the thermodynamic phase of a sulfuric acid aerosol, and due to extreme supercooling of the highly viscous liquid the phase (liquid, glass, crystallite) is a complicated function of the ambient conditions. It was quickly understood that a mechanistic understanding of these reactions was required so that a minimal set of parameters could be used to define the reactivity over the diversity of meteorology characteristic of the upper troposphere and lower stratosphere. Additional difficulties began to emerge due to the morphological complexities of the substrate itself. Major controversies continue in the literature. One concerns the extent to which the internal area of a porous, laboratory grown ice participates in the heterogeneous chemistry.[3]

The paradigm involves addressing successive stages of complexity. In the 1970s, upon consideration of chlorofluorocarbon (CFC) refrigeration technologies, calculations based entirely on homogeneous gas phase reactivity were performed to predict the impact of increased chlorine concentrations in the stratosphere. It was determined that chlorine would be removed in the form of stable compounds such as $ClONO_2$ and $HOCl$ and the impact on ozone would be minimal.[4] With the discovery of the polar ozone hole it was realized that particulate matter in the stratosphere was reactivating chlorine through, among others, the heterogeneous mechanisms 1 and 2.[5] Since incorporation of the first few heterogeneous rate constants into models of the stratosphere, it has become apparent that full reaction mechanisms are required to define a sufficiently broad range of

conditions, and that now the need is for a mechanistic understanding of the chemistry as a function of the full morphological and chemical complexity of the ice substrates.

We have demonstrated the ability to determine the surface localized concentration of several species of interest in the mechanism of 1 and 2. By the application of a surface sensitive spectroscopy, second harmonic generation (SHG), we have succeeded in monitoring the surface thermodynamic phase of HNO_3/H_2O ice.[6] We have observed the condensation of H_2O onto $HNO_3(H_2O)_3$ acid hydrate substrates. We have also observed the adsorption of HCl onto H_2O and $HNO_3(H_2O)_3$ ice. The quantitative nature of the adsorption measurements derives from the ability to distinguish between the ice substrate and the adsorbate, the independent measurement of ice film surface area by physical adsorption, and the quantitative introduction of the adsorbed species as vapor over the ice.

We have developed a model of surface coverage to analyze the adsorption spectra obtained from the second harmonic data, which allow the determination of the mean adsorption energy in both the H_2O on $HNO_3(H_2O)_3$ and HCl on H_2O ice systems. With these tools we have addressed the heterogeneity of the surface molecular potential. We have modeled the considerable data in the literature concerning the reaction probabilities of the heterogeneous reactions 1 and 2 utilizing surface reagent concentrations characterized by surface potentials measured in our laboratory.

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

Prior to the discovery of the so-called "ozone hole," heterogeneous processes were ignored in atmospheric chemistry models. Field measurements, supported by laboratory experiments and modeling, have confirmed the pivotal role of reactions of photoinactive (reservoir) chlorine and nitrogen gases on ice and nitric and sulfuric acid ice aerosols in the Antarctic polar vortex. It was subsequently recognized that the determination of chemical mechanism would be required in order to adequately model the heterogeneous rates as a function of the complex ice surfaces. Attention is now turning to mechanistic studies that incorporate the full thermodynamic and substrate complexity in these systems.

This work builds on a program unique to LANL with the capability to address these questions by probing the complex surface directly. The development of quantitative models of reactivity, which accurately model a wide range of reaction rate data, demonstrates the ability to deconvolute and characterize very complex and

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important heterogeneous chemical systems. This capability is one of the components of the new Atmospheric Sciences Initiative at LANL.

Scientific Approach and Accomplishments

The experimental approach has been built on a technique recently developed at the Laboratory[6] to probe surface chemical composition directly utilizing SHG, a nonlinear surface spectroscopic technique.[7] In general, the application of a high-power laser pulse to a surface results in the conversion of some of the light reflected from the surface to a frequency double that of the input pulse. The efficiency of this conversion process is a function of the chemical composition and thermodynamic phase of the surface. The generation process is also localized to the surface so that the technique represents a direct probe of the surface chemical composition and thermodynamic phase.

We have developed an application of this general technique to probe the molecular surface of transparent, porous ice films in order to characterize reagent concentration and coverage in reactions 1 and 2. We use the 532 nm, 100 μJ pulse from a neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser for scattering from the surface of a porous ice film. We then apply the laser to the sample ice and obtain the doubled-frequency, second-harmonic-generation signal with a solar blind phototube and monochromater detection apparatus. We then introduce the adsorbate gas and monitor the change in second-harmonic generation as a function of surface concentration. Adsorption spectra are shown in Fig. 1 for the adsorption of H_2O on $HNO_3(H_2O)_3$. The adsorbed H_2O serves to mask the second harmonic generation of the underlying substrate and the loss of signal observed as a function of the H_2O concentration is a measure of the amount of the substrate covered.

The dependence of the second harmonic intensity on surface concentration can be expressed as

$$I_{2\omega} = (\chi\theta)^2 \tag{1}$$

where χ is an average second harmonic efficiency and θ is a surface concentration. We apply the Brunauer, Emmett, and Teller (BET) physical adsorption theory in order to model the θ dependence of the SHG signal.[8] From BET theory the total amount of adsorbate on the surface, θ, is given by Equation 2 and the fraction of the total surface area not covered by adsorbate, θ_o, by Equation 3, both in units of monolayers.

$$\theta = \left(\frac{cx}{(1-x)[1+(c-1)x]}\right) \tag{2}$$

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$$\theta_o = \left(1 + \frac{cx}{(1-x)}\right)^{-1} \tag{3}$$

The parameter $c \sim \exp((Q_s - Q_a)/RT)$ depends on the relative adsorbate surface energy Q_s and adsorbate-adsorbate energy Q_a. R is the gas constant and $x = P/P_o$ is the ratio of the vapor pressure to the pressure over the pure phase. The system is fully parameterized by the constant c, relating the amount of material adsorbed, the fractional surface coverage and the pressure.

One interpretation of adsorption data such as shown in Fig. 1 is that adsorption proceeds via multilayer formation, and that $\sqrt{I_{2\omega}}$ is proportional to the fractional amount of substrate covered by adsorbate, irrespective of the depth of coverage, such that $\sqrt{I_{2\omega}} \propto (1-\theta_o)$. Given this interpretation, the isotherms shown as $\sqrt{I_{2\omega}}$ versus coverage in Fig. 1 are equivalent to plotting $(1-\theta_o)$ against θ. By combining equations 2 and 3 and eliminating x, the c constant characterizing the adsorption system within the BET formalism may be directly determined from the spectra. This was the procedure for the calculation of the solid curves of Fig. 1. The shape of the curve is determined entirely by the c constant, with the scattering efficiency, χ, a linear scaling factor used to normalize the signal to one at zero coverage. The value of the c constant, determined by least squares minimization, was 0.006 for H_2O adsorption onto polycrystalline $HNO_3(H_2O)_3$ at 190 K and 0.048 for adsorption at 85 K.

In addition to modeling the adsorption spectra, we have used physical adsorption models to analyze data in the literature from other laboratories concerning the probabilities of reactions 1 and 2 under stratospheric conditions as a function of relative humidity. This model has been described fully in the literature.[9] Briefly, the mechanism of reactivity in reactions 1 and 2 is considered to be prompt reaction between gas phase $ClONO_2$ and adsorbed H_2O or HCl upon collision at the surface, a classic example of the Langmuir-Rideal mechanism.[2] The collision-based probability of reaction, γ, is the parameter typically measured in laboratory studies of reaction 1 and 2. This γ reflects the probability that a reaction will occur upon the collision with the surface by $ClONO_2$. In the context of our collision mechanism, γ is a simple function of the geometric coverage of the surface by either reagent H_2O or Hcl. This probability may be calculated for $ClONO_2 + H_2O$ as

$$\gamma = \gamma_o \, \theta_{H_2O} = \gamma_o(1-\theta_o(c,x)) \tag{4}$$

where γ_o is the reaction probability on a pure H_2O ice. HCl coverage must be calculated on both the H_2O ice and acid hydrate substrate domains for $ClONO_2 + HCl$. In modeling these measurements we follow Tabazadeh and Turco[10] and Mozurkewich[11] and treat HCl

adsorption as a single monolayer process via the Langmuir theory. The probability is then given by

$$\gamma = \gamma_o \, \theta_{HCl} = \gamma_o \left[\frac{\theta_0(c,x) \, K_{ACID}P_{HCl}}{1 + K_{ACID}P_{HCl}} + \frac{(1-\theta_0(c,x)) \sqrt{K_{ICE}P_{HCl}}}{1 + \sqrt{K_{ICE}P_{HCl}}} \right] \quad (5)$$

where θ_{HCl} is the coverage of HCl, K_{ACID} is the Langmuir adsorption constant for HCl on the acid hydrate ice, K_{ICE} is the Langmuir adsorption constant for HCl on H_2O ice, and P_{HCl} is the HCl pressure. The adsorption of HCl is treated as dissociative on H_2O ice and molecular on the acid hydrates, which is the reason for the square root dependence in the second term of Eq. 5. The coverage of the surface as a function of relative humidity is determined by the c constant, which we have measured in our laboratory from spectra such as Fig. 1 for the nitric acid trihydrate (NAT).

We show a comparison of calculations based on these measurements with measured reaction probabilities from other laboratories below. We also show comparison of calculations with data for probabilities over sulfuric acid tetrahydrate ice surfaces (SAT). For these calculations we have fit the c constant for the SAT surface, and derived a value of c=0.2 at 190 K. The data[9] and model calculation for γ as a function of fractional relative humidity for $ClONO_2 + H_2O$ on both sulfuric acid tetrahydrate (SAT, filled data points) and nitric acid trihydrate (NAT, open data points) are shown in Fig. 2. Data for $ClONO_2 + HCl$ are shown in Fig. 3. It is clear that this simple model successfully resolves at least two issues of concern regarding these data that have been expressed in the literature. The difference in reactivity between nitric and sulfuric acid ice substrates is driven by the different adsorption energy of H_2O on each surface. This is indicated by the different c constant for NAT and SAT. The highly nonlinear behavior of reactivity with relative humidity is also resolved as a natural function of the H_2O surface coverage with partial pressure.

The exception to the agreement of the physical adsorption model with the data is for $ClONO_2 + HCl$ on a NAT substrate. The form of the curve for the probability of this reaction is commonly encountered in physical adsorption experiments involving porous media with pore radii in the 10Å to 1000Å range and is characterized as a type IV mesoporous isotherm.[12] The curve reflects enhanced uptake by a porous solid induced by

capillary absorption of liquid solution into the smallest pores. We also propose a reaction mechanism involving reaction in this capillary solution. The data for reaction with HCl are again plotted in Fig. 4. The labeled curve is calculated by reformulating the Kelvin equation as a function of x as

$$V_{HCl} \sim K \left(\frac{dV}{dx}\right)\left(\frac{1}{\ln(x)}\right) \tag{6}$$

where V_{HCl} is the volume of liquid absorbed at x, K is a constant proportional to the surface tension and molar volume of the solution, and dV/dx is a Gaussian function describing the pore distribution in units of volume absorbed at x. The reactivity is then modeled as

$$\gamma = \gamma_o V_{HCl}. \tag{7}$$

In this model increased reactivity with relative humidity arises due to increasing liquid volume as condensation occurs in successively larger pores. We have not yet calculated the absolute volume of liquid involved, which requires the surface tension of the acidic solutions formed on condensation, and the solubility of HCl in such solutions.

The implication of this result is that the reported reaction probability for chlorine nitrate with HCl is actually a measure of reactivity in solution, not a measure of reaction mediated by the surface, and if the physical adsorption model presented here is indicative of the stratospheric process, then the uptake represented by the data for $ClONO_2+HCl$ on NAT may be too large by as much as an order of magnitude.

This last example of interference due to porosity is a prime illustration of the possible difficulties in interpretation of heterogeneous processes that may arise as a function of the complexity of the natural substrate, and highlights the goals of this project. We have shown that by directly measuring surface composition and thermodynamic phase, and by incorporating quantifiably complex features in the surface, such as porosity of known volume and area, it is possible to characterize very complex reaction systems.

Publications

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4. Henson, B. F., K. R. Wilson and Jeanne M. Robinson, "Modeling the Relative Humidity Dependence of Chlorine Nitrate Reactivity on Ices," Talk presented at the 1996 International Symposium of the Physics and Chemistry of Ice, August 1996.

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10. Tabazadeh, A. and R. P. Turco, "A Model for Heterogeneous Chemical Processes on the Surfaces of Ice and Nitric Acid Trihydrate Particles," *J. Geophys. Res.* **98**, 12,727 (1993).

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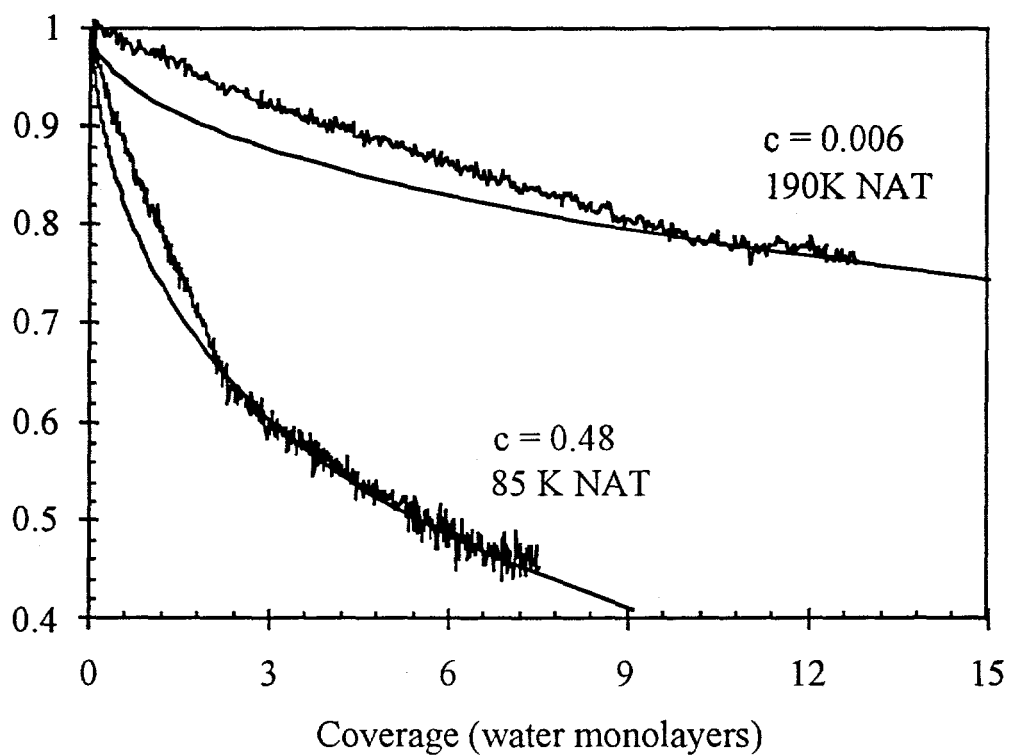12. Adamson, A. W., *The Physical Chemistry of Surfaces* (Wiley, New York, 1990).

Figure 1. Coverage of porous NAT ice film by H_2O at 85 K and 190 K. The data are plotted as the square root of the second harmonic signal against H_2O coverage. The solid curves are fit to the coverage model described in the text. The initial linear dependence arises due to conversion of a monohydrate surface layer to trihydrate.
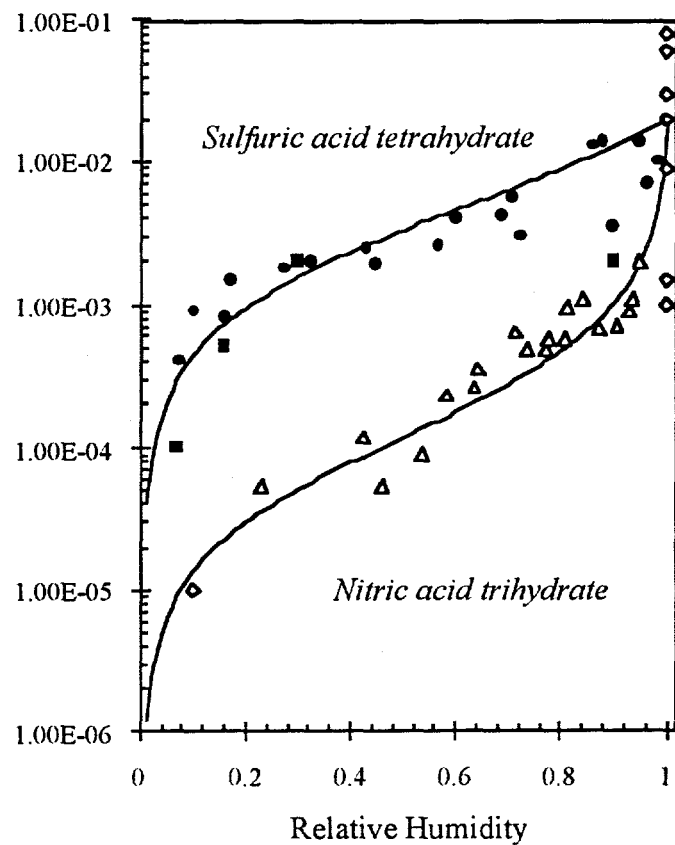
Figure 2. Data for the reaction probability, γ, as a function of relative humidity for the reaction $ClONO_2+H_2O$. Data and model calculations for reaction on SAT (filled points) and NAT (open points) are labeled.
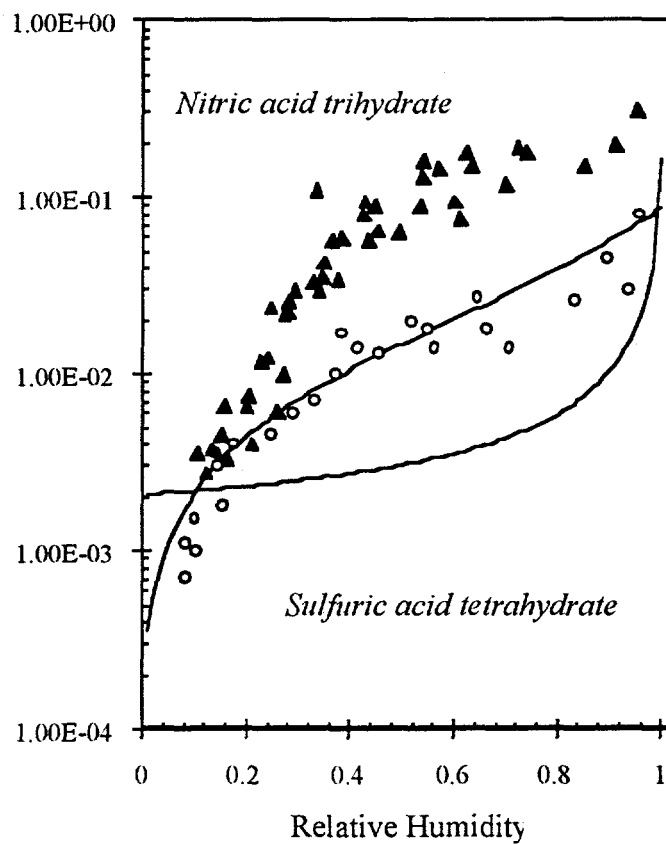
Figure 3. Data for the reaction probability, γ, as a function of relative humidity for the reaction $ClONO_2$+HCl. Data and model calculations for reaction on SAT (filled points) and NAT (open points) are labeled.

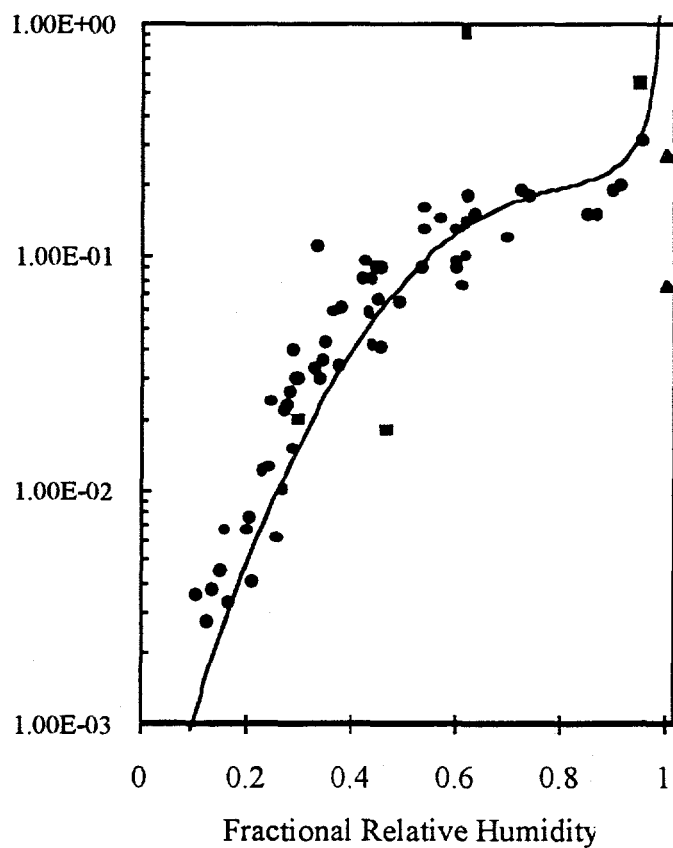Figure 4. Data for the reaction probability, γ, as a function of relative humidity for the reaction $ClONO_2 + HCl$ on NAT. Model calculation of reaction probability is based on the capillary absorption mechanism discussed in the text.

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