A Low-Temperature Infrared Study of the Reactions of the Stratospheric NO_y Reservoir Species Dinitrogen Pentoxide with Water Ice, 80–160 K

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The low-temperature chemistry of thin films of water ice and the important stratospheric NO_y species dinitrogen pentoxide have been investigated in order to spectroscopically characterize one of the principal heterogeneous reactions that occurs on polar stratospheric cloud particles (PSCs). This contributes to stratospheric denitrification. Using reflection–absorption infrared spectroscopy, we have observed the formation of both covalent and ionic forms of solid N_2O_5 on both ice and the clean substrate. Thermal evolution experiments suggest that the solid covalent phase, which can only be formed at the lowest temperatures ($T < 100$ K), is metastable with respect to the ionic phase. However, we observe no reaction between the solid ionic form and the pure ice film at $T < 170$ K. Reaction does occur above 140 K between the ice film and gas-phase covalent N_2O_5 to form a surface layer of hydroxonium ions, solvated nitrate ions, and molecular nitric acid. Annealing to 160 K introduces more water into the surface layer by diffusion and produces a further reaction of the excess NO_2^+ and results in the formation of more molecular nitric acid. Some of the water reacts with molecular nitric acid to form an amorphous hydrate $(H_2O)_n{\cdot}H_3O^+NO_3^-$. From this, we conclude that only N_2O_5 in the gas-phase covalent form reacts readily with ice and consequently that the reaction in the stratosphere is likely to involve the interaction between the gas phase and the ice surface and not a solid–solid interfacial one. The reaction of gas-phase N_2O_5 with a nitrate-containing ice surface and the competition between surface species for excess water has important implications for different N_2O_5 chemistry on type I (NAT) and type II (ice) PSC particles.

Introduction

It is now well established that the primary perturbation of stratospheric ozone chemistry is due to localized heterogeneous interactions combined with meteorological and photolytic phenomena over the polar regions.[1–5] These interactions are observed to occur in areas where particulate concentration is high. Of primary interest are polar stratospheric clouds (PSCs), which form as the temperature drops during winter. PSCs are usually divided into two main groups. Type I PSCs form as small crystals of nitric acid trihydrate at 5–7 K above the ice frost point. Below the frost point, these particles act as nucleation centers for the condensation of type II PSCs which are essentially small ice crystals. Heterogeneous interactions of chlorine-, bromine-, and nitrogen-containing species (HCl, HBr, $ClONO_2$, N_2O_5, etc.) on PSC particles and aerosol droplets lead to a repartitioning of the chlorine and bromine from stable, reservoir forms into more reactive species which can then interfere with ozone chemistry. The loss of N_2O_5 from the stratosphere and the resultant formation of more nitric acid also affects the balance of active chlorine by removal of one of the gas-phase ClO_x sequestering channels. This nitric acid may also then be incorporated into further PSC particles or lost through precipitation. Studies of the heterogeneous chemistry of ice and acid hydrate films are therefore vital to the understanding of the nature and availability of active ozone depleting species (Cl atoms, ClO, *etc.*) as well as the nitrogen chemistry of the stratosphere.

Some of the principal reactions of N_2O_5 which are thought to be catalyzed in the presence of cold surfaces in the stratosphere are shown below:

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3$$

$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$$

$$N_2O_5 + HBr \rightarrow BrNO_2 + HNO_3$$

In this paper, we describe a series of experiments in which we have investigated the reaction of dinitrogen pentoxide with ice films under a variety of conditions. We observe a distinct difference in reactivity that depends not only upon the amount of available water but also on the physical form of the N_2O_5.

Experimental Section

Spectroscopic studies were performed *in situ* in a cylindrical stainless steel chamber pumped by a oil-vapor diffusion pump and a liquid nitrogen cooled cryoshield with an approximate area of 1 m^2. The vacuum system is optically coupled to a Bio-Rad FT infrared spectrometer (Model FTS60A/896) using aluminum mirror transfer optics and vacuum compatible KBr windows to focus the IR beam at the sample position at an angle of 75° to the surface normal. The reflected beam is detected using a HgCdTe photoconductive detector cooled to 77 K.

The substrate upon which ice films are condensed consists of a flat foil of gold or nickel mounted between a pair of tungsten supports. These supports are in thermal contact with a liquid nitrogen reservoir. The temperature is controlled by balancing the reservoir cooling against the resistively heated foil. The substrate temperature is measured with a chromel/alumel thermocouple, spot-welded directly to the foil substrate, and can be varied between 80 and 1000 K with a stability of ±0.5 K. The sample is supported in the vacuum chamber on the end of an (x, y, z, θ) manipulator.

Sample gases are dosed into the vacuum chamber *via* a pulsed dosing system which consists of three independent gas reservoirs to ensure sample purity. Each reservoir can be filled with either pure gases or a carefully controlled mixture. Absolute pressure measurement using capacitance manometers (MKS Baratron) ensures accurate mixing ratios. Each reservoir is connected to the vacuum system via a piezoelectric pulsed valve (LaserTechnics LPV) controlled by in-house electronics that provide a pulse of gas at the reservoir pressure with a mean width of between 50 μs and 2 ms. One of the gas lines is also fitted with a precision leak valve (Fisons Instruments MD6) for controlled-rate effusive dosing onto the substrate. Gas samples inside the chamber are directed at the sample position by glass guide tubes. Vacuum pressure and gas composition measurements inside the vacuum

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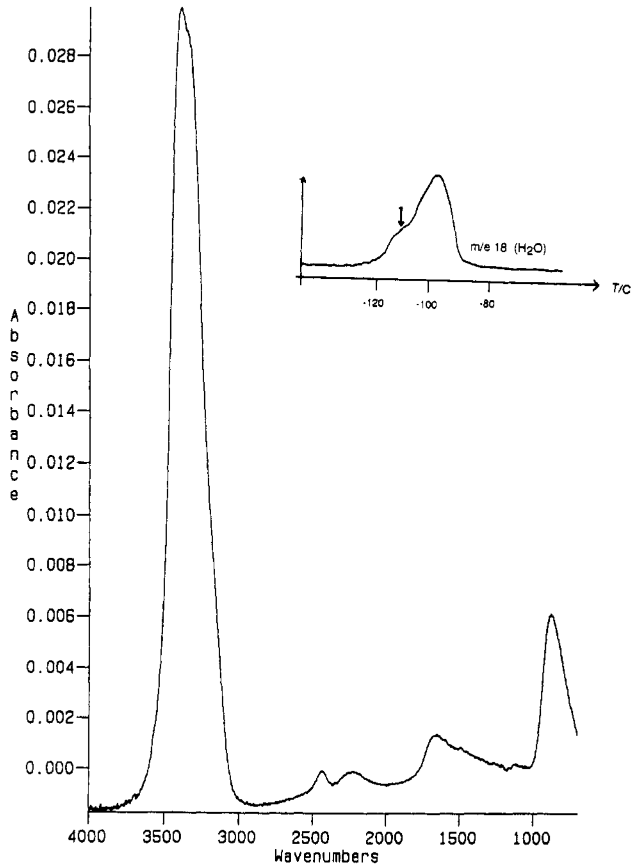


Figure 1. RAIR spectrum of a typical thin water layer at 80 K, formed by depositing water from the gas phase onto a cold foil and annealing to the low-temperature desorption shoulder (inset TDS).

chamber were made using an MKS cold cathode ionization gauge and a 200 amu range quadrupole mass spectrometer (Spectramass DataQuad).

Ice films were grown using pure water by slow effusive leak onto the cold substrate. Spectroscopic characterization indicated that the films could be formed at a variety of temperatures with good reproducibility. Dinitrogen pentoxide (N_2O_5) was prepared by the gas phase reaction of ozone (O_3) with either nitric oxide (NO) (BDH 99%) or nitrogen dioxide (NO_2) (BDH 99.5%).[6] O_3 was synthesized by passing zero grade oxygen through a commercial ozonizer. The final product was thoroughly degassed at 195 K to remove excess O_2 and O_3 and stored in the dark at 77 K. The gas-phase FTIR spectrum of the product corresponds well to other published spectra[7] with a trace contamination of nitrogen dioxide (Figure 2, trace A).

Results

Ice films were grown using a standardized methodology for reproducibility, developed by monitoring the solid ice film and the gas phase above it from deposition at 80 K using infrared spectroscopy and thermal desorption spectrometry. The standard procedure finally adopted for low-temperature studies involves ice deposition from a pressure of 1×10^{-7} mbar water for 60 s at 80 K. Although we are not able to measure film thickness accurately, the integrated intensity of the OH stretching modes in the infrared spectrum suggests that the films are of the order of 50 nm thick. Exact dose reproducibility was ensured by integrating the area under the m/e 18 trace of the mass spectrometer during exposure. The film is subsequently heated until the partial pressure of water (as measured by the mass spectrometer) starts to rise. This onset of desorption corresponds to the low-temperature shoulder in the thermal desorption spectrum shown in Figure 1 (inset), which is due to the film ordering into a more crystalline state. At this point, the substrate temperature is held constant until the water partial pressure starts to fall. The substrate is then cooled to the required temperature. Figure 1 shows the typical spectrum obtained for an H_2O film grown under these conditions and recooled to 80 K.

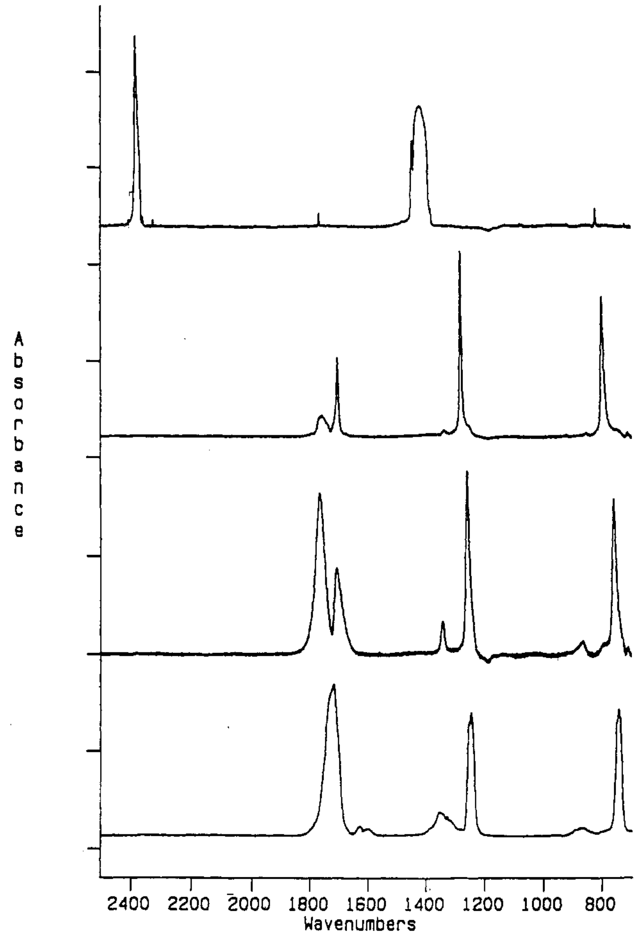


Figure 2. RAIR spectra of thin N_2O_5 films of a cold foil substrate: from the bottom (A) gas phase, 1 mbar N_2O_5 in a 10-cm gas cell; (B) N_2O_5 film deposited at 80 K; (C) N_2O_5 film deposited at 80 K and annealed to 100 K; (D) N_2O_5 film deposited at 120 K, showing the ionic $NO_2^+NO_3^-$ structure.

We have studied the low-temperature deposition of N_2O_5 on thin ice films and on the bare substrate. Between 80 and 120 K, we did not observe any difference in N_2O_5 behavior on either the ice film or the bare substrate. The spectrum of N_2O_5 deposited on a nickel foil at 80 K is shown in the Figure 2, trace B. The spectrum is qualitatively similar to the gas-phase spectrum (Figure 2, trace A). Annealing to, or direct deposition at, 100 K gives the spectrum in Figure 2C. At 100 K, the spectrum undergoes irreversible conversion to Figure 2D over a period of several hours. This transformation is also observed to occur more rapidly under further annealing, and the film eventually desorbs above 160 K. Adsorption above 120 K results in the direct formation of Figure 2D. Reference spectra in the literature facilitate the assignment of these species to solid amorphous covalent, solid crystalline covalent, and solid ionic N_2O_5.[8,9]

Deposition of N_2O_5 from a dosing pressure of 1×10^{-7} mbar onto an ice film at 120 K gives the spectrum in Figure 3A, which is simply a composite of pure water and pure solid ionic N_2O_5. Slow annealing of this bilayer film to 160 K results in the desorption of most of the water layer through the N_2O_5 overlayer, Figure 3B. Above 160 K, the N_2O_5 desorbs leaving a clean surface. Deposition of a thin ice film on top of a solid film of covalent N_2O_5 at 80 K also gives a composite spectrum. Annealing to 120 K forms the same spectrum as Figure 3A. Further annealing

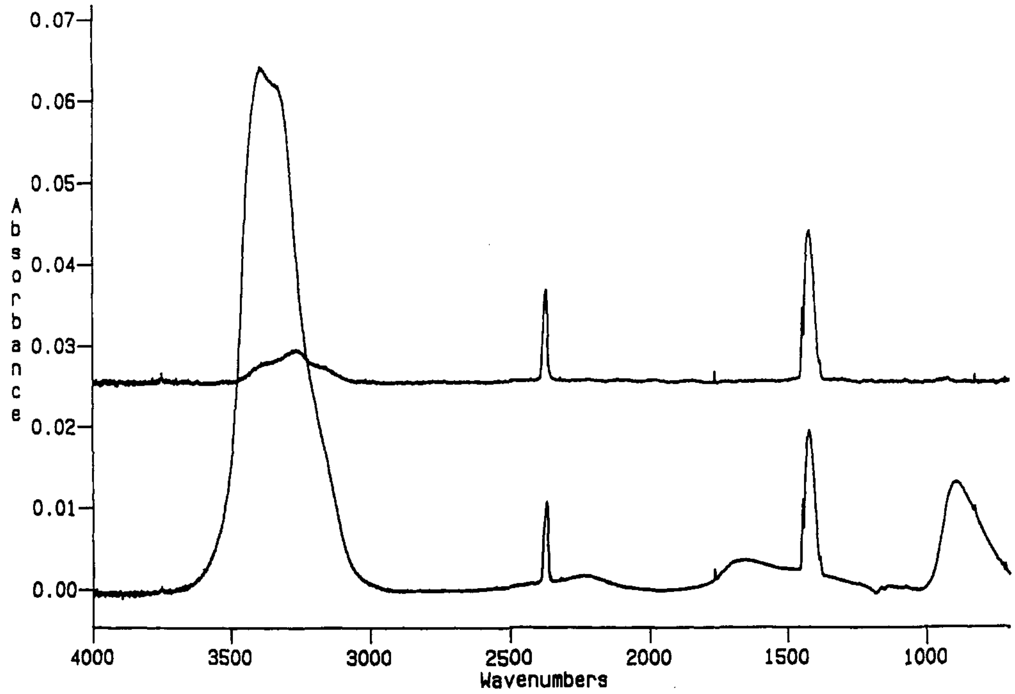


Figure 3. RAIR spectra of the deposition of a thin N_2O_5 layer on an ice film: (A, lower) as grown at 120 K; (B, upper) annealed to 160 K.

results once again in the evaporation of both layers without reaction.

The reaction of increasing doses of gas-phase covalent N_2O_5 with a thin ice film at 140 K is shown in Figure 4. These are absorbance difference specta in which negative bands correspond to losses from the original film and positive bands to reaction products. At low doses, the first observation is a water loss, evidenced by the negative bands at *ca.* 3400, 1600, and 800 cm^{-1}. Concurrently, strong broad features centered on *ca.* 2900 and 1750 cm^{-1} and sharper bands at *ca.* 1450, 1300, 1040, and 810 cm^{-1} start to grow in, labeled species A and B, respectively. Increasing doses result in further water loss and new features at 2380 cm^{-1} (species C) and 1682, 1318, 965, and 778 cm^{-1} (species D).

Subsequent annealing of the saturated film results in a further change in the spectrum, shown in Figure 5. Further ice is lost, as is the species C absorption, and the features due to species A and B strengthen. Annealing above 180 K results in the loss of all spectral features.

Discussion

Low-Temperature Solid N_2O_5 Film Behavior. The condensation of N_2O_5 at 80 K results in the formation of a solid amorphous film with a spectrum similar to that of the gas phase. This is the well-documented covalent form shown in Figure 6. The molecule is planar with C_{2v} symmetry. As previously reported, the central N–O–N bond allows the coupling of the nitro group vibrations to produce in-phase and out-of-phase NO_2 modes. The strong features at 1764 and 1705 cm^{-1} can therefore be assigned to the out-of-phase and in-phase asymmetric stretch and those at 1340 and 1258 cm^{-1} to the out-of-phase and in-phase symmetric stretch. The nitro symmetric deformation at 760 cm^{-1} does not appear to be split. The remaining band at 864 cm^{-1} is the skeletal N–O–N asymmetric stretch. The bands and their symmetries under C_{2v} are tabulated in Table 1. It should be noted that the frequencies we observe are blue-shifted from other published solid-phase spectra. The origin of this shift is as yet undetermined. When this amorphous film is annealed to 100 K, it is irreversibly transformed into a more ordered crystalline structure. This has also been observed for the condensed solid on KBr. However, in this system we have the presence of a metal surface which imposes a vertical polarization in the surface standing wave of the incident radiation to distances of the order of the wavelength. It can clearly be seen that it is the B_2 modes that are reduced severely in intensity. This can be explained most simply if the molecules are aligned with their plane perpendicular to the metal surface. Under such an alignment, the B_2 vibrations which give rise to a dipole change parallel to the surface are forbidden. Figure 7 illustrates the effect for the four nitro stretches.

TABLE 1

gas	solid			assignment	symmetry in C_{2v}
	80 K	100 K	120 K		
–	–	–	2386 (vs)	ν_{asym} linear $O{=}N{=}O^+$	–
1718 (s)	1764 (s)	1752 (w)	–	ν_{asym} NO_2	A_1
–	–	–	1420 (s)	ν_{asym} NO_3^-	–
1326 (w)	1340 (w)	1337 (w)	–	ν_{sym} NO_2	B_2
1246 (s)	1258 (s)	1280 (s)	–	ν_{sym} NO_2	A_1
868 (w)	864 (w)	854 (vw)	–	ν_{asym} NON	B_2
744 (s)	760 (s)	798 (s)	–	δ_{sym} NO_2	A_1

The layer undergoes a further irreversible transformation into the ionic nitronium nitrate structure. The conversion at 100 K occurs over a period of 2–4 hours, whereas the film showed no tendencies to ionize at 80 K over a period of 8 h. This suggests that the solid covalent structure is metastable with respect to the ionic form. The X-ray crystal structure of solid ionic N_2O_5 shows the $O{=}N{=}O^+$ unit to be linear and NO_3^- unit to be planar. The strong band at 2386 cm^{-1} is therefore assigned to the asymmetric NO_2^+ stretch and the broad band centered on 1420 cm^{-1} to the asymmetric NO_3^- stretch. By analogy with the isoelectronic CO_2 molecule, we would expect the NO_2^+ deformation to occur below 700 cm^{-1}, a region where our detector has no sensitivity.

Solid-State Reaction of N_2O_5 with Ice below 160 K. There appears to be no reaction of solid ionic N_2O_5 with ice at temperatures below 160 K, even after holding the film for a period of several hours. The lack of reactivity of the ionic form is highlighted by the fact that most of the water layer, either underlying or overlying the N_2O_5 film, can evaporate without reaction. For the N_2O_5 overlayer case, the water vapor must desorb through the overlayer, presumably by diffusing along grain boundaries between the N_2O_5 crystallites. The spectrum in Figure 3 shows a small water absorption underlying the strong N_2O_5

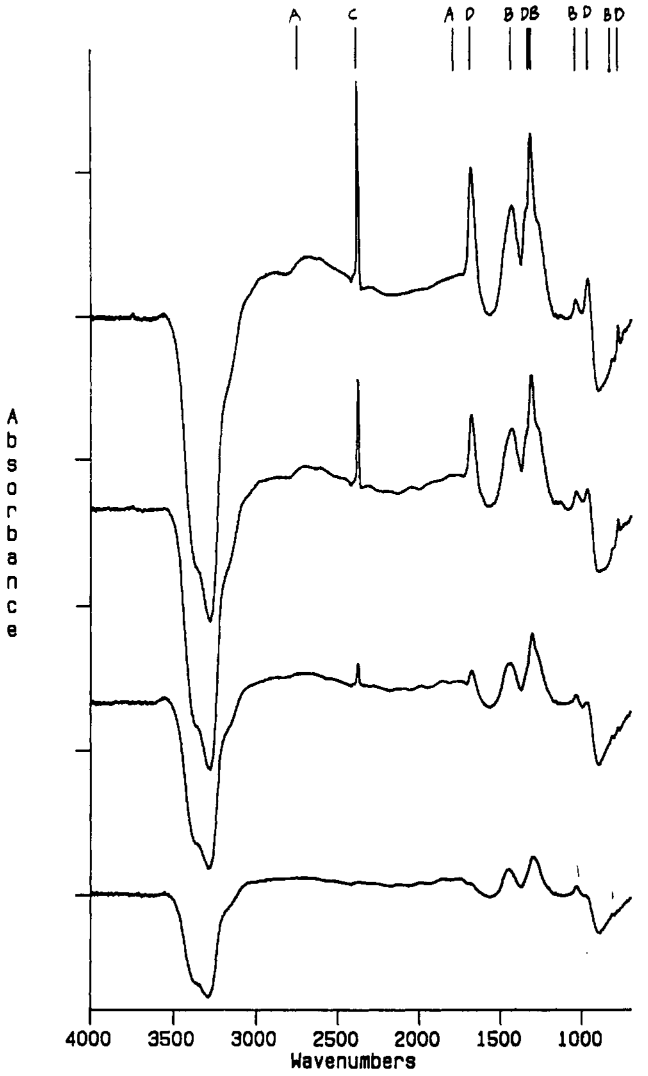


Figure 4. RAIR difference spectra of successive doses of N_2O_5 onto an ice film at 140 K, with the clean, annealed ice film as background. From the bottom (A) first-stage buildup of the amorphous hydrate; (B) onset of molecular nitric acid growth; (C) high exposure, showing nitronium, hydroxonium, and molecular nitric acid in addition to the amorphous hydrate.

spectrum, which we believe to be a thin, interfacial layer of water physically adsorbed on the surface of N_2O_5 crystallites. There is no evidence for any hydrate formation.

TABLE 2

matrix-isolated nitric acid[15]	ionic N_2O_5	A, H_3O^+	B, NO_3^-	C, NO_2^+	D, $HONO_2$
		2900			
	2386			2380	
1670		1750			1682
	-1420 (b)		-1450		
1305			~1300		1318
			1040		
947					965
770			810		778

Reactions with One Gas-Phase and One Solid Reactant. When a solid layer of ionic N_2O_5 is exposed to gas-phase water from the dosing lines at temperatures between 80 and 160 K, no reaction is observed other than the deposition of a layer of ice on top of the N_2O_5. However, when gas-phase covalent N_2O_5 is dosed onto the surface of an ice film at 140 K, the formation of a number of new bands is observed as a function of exposure. Initially, two groups of strong features are observed (species A and B). By comparison with literature spectra of hydrated acid ices,[10-15] species A can be identified as being a hydronium ion. Species B is assigned to a solvated nitrate ion for which the bands at *ca.* 1450 and 1300 cm^{-1} are the two components of the normally degenerate asymmetric stretching mode, where the degeneracy is lifted due to the low symmetry of the planar nitrate environment. The weak feature at 1040 cm^{-1} is the formally forbidden symmetric stretch which is often observed in disordered films. The weak feature at 810 cm^{-1} is the NO_3^- bending mode. The presence of species A and B are evidence for the formation of an amorphous nitric acid hydrate, for which we propose the reaction scheme

$$N_2O_5 + nH_2O \rightarrow 2HONO_2 + (n-1)H_2O \rightarrow 2H_3O^+NO_3^-\cdot(n-3)H_2O$$

The number of water molecules, n, involved in the reaction will be determined principally by the preferred stoichiometry of the hydrate formed, *i.e.*, NAT, NAM, *etc.*, and the availability of water in the region of reaction. Studies of the formation of nitric acid hydrates as a function of temperature suggest that the monohydrate and the dihydrate may be favored at 140 K.[11] However, we are unable to unequivocally assign our spectra as anything other than an amorphous hydrate. As the amount of surface water available for reaction is reduced on further dosing of N_2O_5, a change occurs with the simultaneous growth of species C and D. By comparison with the solid N_2O_5 film spectra, species C can be assigned to linear NO_2^+. The remaining bands (species D) are due to molecular nitric acid, confirmed by comparison with matrix-isolated nitric acid at 4.2 K.[15] The formation of molecular nitric acid as the amount of available surface water decreases is not surprising. From the point at which the formation of the amorphous nitric acid hydrate reaches a saturation coverage, further reaction requires that either diffusion of the water to the surface occurs to release more water or that the reaction scheme must change. Our spectra suggest that the latter is the case. Since the bands due to the nitronium ion and molecular nitric acid grow in together, it seems likely that they are formed concurrently from the partial hydrolysis of gas phase N_2O_5 as it impinges upon the surface. Considering the likely surface species in the saturated layer (NO_2^+, H_3O^+, $HONO_2$, *etc.*) and the scarcity of water, it seems likely that the hydrolysis occurs by reaction of N_2O_5 not with water but rather with the hydroxonium ion. The products from such a reaction would be $HONO_2$, water, and NO_2^+.

$$N_2O_5 + H_3O^+ \rightarrow HONO_2 + NO_2^+ + H_2O$$

This generation of more surface water, able to undergo further reaction with N_2O_5 to produce more partially hydrated nitric acid and therefore more nitrate ions, accounts for the growth of the nitrate bands during the formation of molecular nitric acid. The band positions and assignments for species A, B, C, and D are summarized in Table 2.

Annealing this composite film to 160 K results in the production of a thicker film of molecular nitric acid and a small amount of nitric acid hydrate. This occurs because the increase in mobility of the ice film allows water to diffuse. As more water becomes available for reaction with the molecular nitric acid and NO_2^+, further changes occur. NO_2^+ and water are both consumed to produce more nitric acid and a proton. The proton becomes hydrated and this can be seen in the growth of the broad H_3O^+ absorption in the difference spectrum (Figure 5). The charge associated with this ion is balanced by the negative charge on the nitrate ion originally associated with the NO_2^+, thus maintaining overall neutrality. The fact that there is only a slight increase in the nitrate ion absorptions indicates that the rate of solvation of molecular nitric acid is slower than that for reaction of the nitronium ion. Annealing above 180 K results in the loss by evaporation of this film.

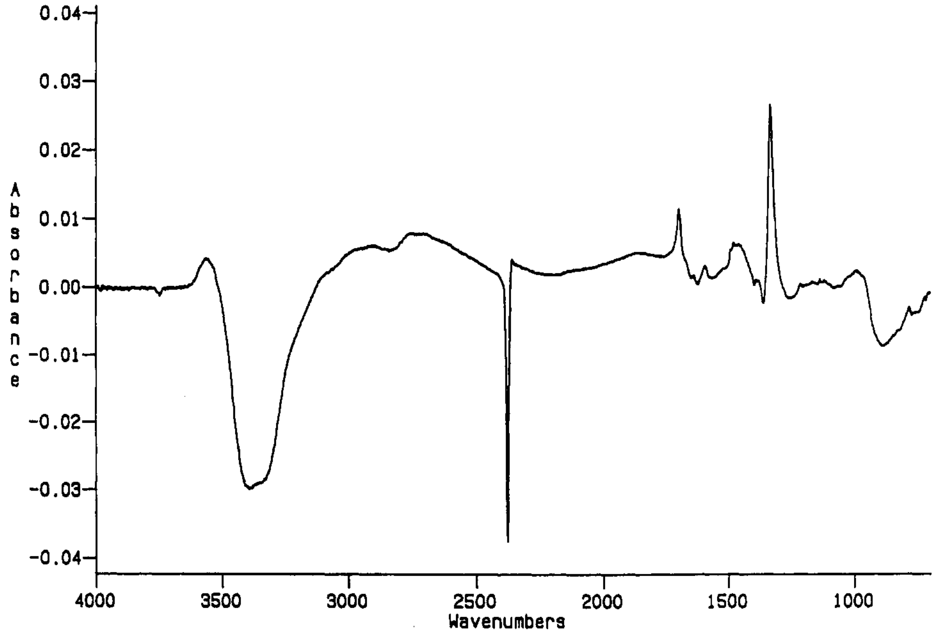
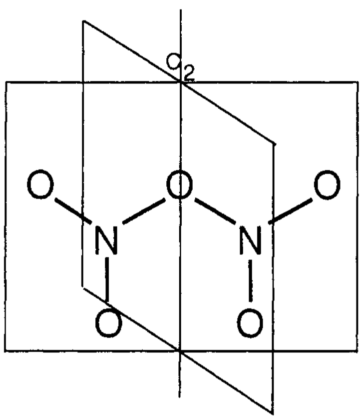


Figure 5. RAIR difference spectrum of the result of annealing the film shown in Figure 4A to 160 K with 4A as a background, showing the growth of molecular nitric acid and hydroxonium ion and the loss of water and nitronium ion.

(A) Covalent molecular N_2O_5



(B) ionic molecular N_2O_5

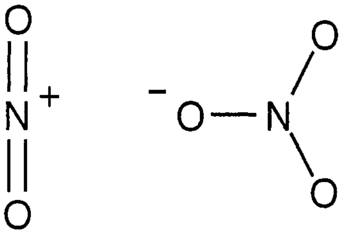
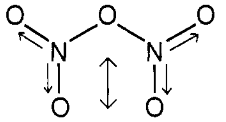
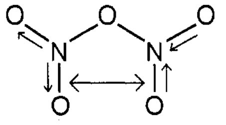


Figure 6. Structure of solid N_2O_5 (A) covalent from (B) ionic form.

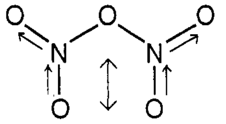
(A) In-phase, symmetric stretch, A_1



(B) Out-of-phase symmetric stretch, B_2



(C) In-phase asymmetric stretch, A_1



(D) Out-of-phase asymmetric stretch, B_2

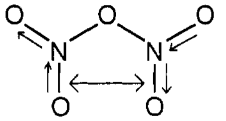


Figure 7. Dipole changes and symmetries for the in-phase and out-of-phase symmetric and asymmetric nitro group stretches, showing the direction of polarization for the parallel and perpendicular modes.

To summarize, the reaction of gas-phase N_2O_5 with a thin ice film occurs through a complex interplay of ionic chemistry involving nitrate, nitronium, and hydroxonium species, for which we suggest the following scheme:

$$N_2O_5 + 3H_2O \rightarrow 2NO_3^- + 2H_3O^+ \quad (1)$$

$$H_3O^+ + N_2O_5 \rightarrow HONO_2 + NO_2^+ + H_2O \quad (2)$$

$$2H_2O + NO_2^+ \rightarrow HONO_2 + H_3O^+ \quad (3)$$

$$HONO_2 + H_2O \rightarrow NO_3^- + H_3O^+ \quad (4)$$

$$\text{overall} \quad 2N_2O_5 + 6H_2O \rightarrow 4NO_3^- + 4H_3O^+$$

During the initial uptake, reaction 1 prevails until saturation occurs. Beyond this limit, dictated by the water availability which prevents complete hydration of NO_2^+ and nitric acid and effectively eliminates steps 3 and 4, there is a competition between nitrogen-containing entities for the surface water. N_2O_5 arriving from the gas phase forms molecular nitric acid and NO_2^+ from the hydrolysis of N_2O_5 on the hydroxonium-rich surface reaction 2. The charge balance is maintained by the presence of the NO_3^- counterion released by the reaction of its accompanying hydroxonium ion. On annealing, more water becomes available as the ice film becomes mobile and is consumed by the above reaction scheme to reduce the concentration of NO_2^+ which produces more molecular nitric acid and hydroxonium species. There is a competition between the NO_2^+ and the molecular nitric acid for the water in steps 3 and 4, and our observation that the NO_2^+ band is depleted and more $HONO_2$ is formed suggests that (3) occurs in preference to (4). The pH of the surface layer is likely to control the relative contributions of these four surface reactions and further investigation is in progress.

Conclusion

The condensation of N_2O_5 on both a cold, unreactive substrate and on ice indicates that there is a strong tendency in the metastable covalent solid for the molecules to order with their C_2 axes perpendicular to the plane of the surface. At higher temperatures, a stable ionic solid with no obvious orientation is formed. There is no detectable reaction between solid ionic N_2O_5 and either solid or gaseous water below 160 K.

The difference in reactivity between ionic and covalent N_2O_5 has several implications for stratospheric chemistry, as does the difference between pure ice films and NO_y-containing layers. It seems likely that the reactivity of N_2O_5 from the gas phase with NAT particles will be completely different from that with ice particles in the early stages of their formation, where they may be largely uncontaminated. Under stratospheric conditions, the partial pressure of N_2O_5 is low and the situation will constantly be in the low-exposure regime, far away from saturation coverage and hence reaction 1 will prevail. On NAT particles however, the reaction of N_2O_5 will dehydrate the surface even further and reactions 2 and 3 will prevail. The chemisorption of other stratospheric gases such as HCl which rely upon solvation of the ionic products by surface water[16,17] may be expected to be influenced by coadsorption with N_2O_5. The apparently rapid reaction of N_2O_5 with ice surfaces at stratospheric temperatures also implies that molecular N_2O_5 is unlikely to play a major role in heterogenous reactions but will rather react through its decomposition and water reaction products nitric acid, NO_2^+, NO_3^-, and hydroxonium species at the surface of ice and NAT particles. The availability of surface water and likely surface pH dependence of the reaction products also has implications for the processing of N_2O_5 by sulfuric acid aerosol, where it is possible that the low surface pH and the high mobility of water within such liquid particles may lead to higher reactivity towards N_2O_5 by adjusting the reaction stoichiometry favored by water excess at the surface.

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