A-1.3.4 Experimental Research on Chlorine Molecule Productivity of the Stratospheric Aerosols

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Stratospheric aerosol testing chember were assembled for diagnosing the heterogeneous reactions on polar stratospheric clouds (PSCs). At first, the chamber were tested of its performances and thereafter, we made some of modeled PSCs films composed from nitric-acid and water. We made also cooling test of liquid nitric-acid / water, sulfuric-acid / water and sulfuric-acid / nitric-acid / water solutions which is thought as precursor of PSCs.

The performance of the chamber were tested of its tempereture stability at 183K, of its property for leak and of gas purging property of optical pass of Fourier transformation infrared (FTIR) spectrometer. Resulting data indicated that the chamber has an ability to produce modeled PSCs.

Using nitric acid and water vapor, depositted solid films on KRS-5 substrate were characterized by infrared absorption spectra to ice, α-nitric acid trihydrate (NAT), β-NAT, nitric acid dihydrate (NAD), nitric acid monohydrate (NAM), and their amorphas phase from comparing with previous works of Ritzhaupt and Devlin,(1991) and Koehler et al.,(1992). As NAD and α-NAT changed into β-NAT phase during heating, it was expected that β-NAT is the most pronounced phase of end of the polar storartospheric winter

The infrared and urtraviolet spectra of liquid nitric-acid / sulfuric-acid / water films upon cooling indicated that few percentages of nitric acid caused disappearnce of water absorption peaks and 10% of sulfuric acid depressed freezing point of a solution more than 10K and caused absorption spectral peak toward high energy region.

1. Introduction

Ozonsou kansoku houkoku : 1993 (Japan Meteorological Agency, 1994) reported that the amunt of decomposed antarctic strarospheric ozone reached about 77Mt in September of 1993. That was 5% of stratospheric ozone of southern hemisphere, and twice amount of level of decade ago. Solomon et al. (1986) suggested that heterogeneous reactions on polar stratospheric clouds (PSCs) which convert halogene reservoir molecules (ClONO2 and HCl) into photoactive molecules (Cl2 and HOCl) are responsible for polar stratospheric ozone hole.. Heterogeneous reactions on PSCs also can convert NOx which can trap ClO as ClONO2 into HNO3 that mouch inactive species. Many observation were conducted at both polar stratospheric resions (i.e. NOSE, AAOE, AASE, AASE **II**, SESAMI). Their results shows that the heterogeneous reactions on PSCs are responsible for ozone destruction.

Two distinct types of PSCs have been proposed: type **I** PSC formes at some tempereture above the frost point, and type **II** PSC forms at the frost point. The latter contains water ice from its formed temperature. As Type **I** PSC contains large amounts of nitric acid from observation, its phase and composition is suggested as nitric acid trihydrate (NAT) (Toon et al., 1986, Hanson and Mauersberger, 1988), nitric acid dihydrate (NAD) (Ritzhaupt and Devlin, 1991, Worsnop et. al., 1993), supercooled binary HNO3-H2O solution (SBS) (Hanson, 1990) and supercooled ternary HNO3-H2SO4-H2O solution (STS) (Zhang et al., 1993). At least, PSCs containning H2O and nitric acid, so these materials must be needed to investigate of their role for stratospheric ozone destruction.

2. Research Objective

The goal of this research is to quantify the role of PSCs to polar stratospheric ozone decomposition. To reach the goal, some step are needed. The first step is to compose PSCs in raboratory. Second step is to investigate heterogeneous reactions on modeled PSCs. Third step is to apply the experimental results to real stratosperic condition and diagonizing the results. As seen later, we have done the first step of this research, and that approach and results will be noted as follows.

3. Research Method

For studing heterogeneous reactions on surface of PSCs, it is needed to form nitric acid hydrates under mimic conditions as polar stratosphere. For this objective, we equipped an chamber named stratospheric aerozol testing chamber (Fig. 1), and tested of its properties of stability of gas pressure and cold tempereture, and of water vapour purging property of infrared optical passway. Modeled PSCs were depositted from gas phase to surface of KRS-5 substrate which is installed inside of the chamber and is also installed across optical layout of Fourier transformation infrared (FTIR) spectrometer. The infrared absorption spectra of nitric-acid / ice films, representative of PSCs were mesured under mimic temperature and pressure conditions of the polar stratospheric winter, and were characterised by comparing with previous works of Ritzhaupt and Devlin,(1991) and Koehler et al.,(1992).

We studied also spectral property of liquid nitric acid and sulfuric acid under cooling condition. Infrared (IR) and urtraviolet (UV) absorption spectra of these samples were obtained using IR and UV spectrometer, and analised. As water containing liquid have large optigai thickness in IR spectral region, sample were prepared among two KRS-5 windows which is placed 10μm each other by spacer.

4. Result

4.1 Results of test of the stratospheric aerozol testing chamber

From Fig. 2 to Fig. 4 are result of cooling test, gas pressure stability test and water vapour purging property of FTIR optical passway, respectively. We could hold tempereture of KRS–5 substrate about 183K more than 2 hours. We could also hold pressure of chamber below that of lower stratosphere more than 1 month. Using N2 gas for purging of FTIR optical passway, almost of water vapour was purged. We concluded that the chamber is useful for formation of modeled PSCs.

4.2 Formation and phase transformation of modeled PSCs

Using appropriate pressure of water vapour and nitric acid to cooled stratospheric aerosol testing chamber, we could obtaine a series of absorption spectra as shown in Fig. 5. From the knowlidge of previous works of Ritzhaupt and Devlin (1991) and Koehler et al. (1992), these spectra were assigned as follows ; at first, amorphas film of stoichiometry of NAD (hereafter we denote amorphas as a–, so this case is written as a–NAD) was deposítted, and thereafter it crystallize into NAD, and finaly, it changed into β–NAT. By changing water vapour and nitric acid pressure, we could get several kinds of nitric acid hydrate as shown in Fig. 6. Phase transformation also observed in many case especially during annealing the film. Observed phase transformation are as follows ;

a–NAM → NAM
a–NAD → NAD → β–NAT
ice + HNO3(g) → ice + α–NAT → β–NAT

We couldn't observed opposit direction of phase transfoemation, so it's concluded that when nitric acid concentration is not so high, formed solid containning nitric acid has a tendency to transform into β–NAT.

4.3 Spectral property of cooled nitric and sulfuric acid

IR spectra of during cooling water, 1 wt % nitric acid / water solution and 10 wt % sulfuric acid / water solution are shown in Fig. 7, 8 and Fig. 9, respectively. OH streching vibrational mode was regulated markedly in nitric acid containning solution.

UV spectra of 1 wt % nitric acid / water solution and 10 wt % sulfuric acid / water solution are shown in Fig. 10 and 11, respectively. UV spectrum of H2SO4, 48.5 wt % / HNO3, 1 wt % / H2O, 50.5 wt % ternary solution also shown in Fig. 11. A n–π* absorption peak of nitric acid hydrate ion (H3O+NO3–) was shifted by adding sulfuric acid as shown in Table 1.

Table 1 Variation in n–π* absorption wavelength for the sulfuric acid – nitric acid – water terneary system.

Component (%)			n–π* absorption (nm)
H2SO4	HNO3	H2O	
0	1	99	301.0
10	1	89	298.5
30	1	69	288.0
48.5	1	50.5	268.5
67.5	1	31.1	263.0

5. Discussion

According to phase diagram of nitric acid and water vapour (e. g. Hanson and Mauersberger, 1988, Molina, 1994), NAM and NAT only are depicted as stable phase. But, many researchers (e. g. Ritzhaupt and Devlin, 1991, Koehler et al., 1992, Worsnop et al., 1993, Hanson and Ravishankara, 1993, Middlebrook et al., 1994, Wooldridge et al., 1995) have reported that NAD was composed under polar stratospheric conditions. We also got sometimes FTIR spectrum of NAD, so it may be pronounced phase under some condition of beginning of formation of PSCs. We have also observed NAD converted into β–NAT same as many researchers.

The direction of phase transformation of modeled PSCs composed from nitric acid and water vapour, under polar stratospheric condition is reported by Koehler et al., (1992). They reported amorphas firm are crystallized irreversibly, and α–NAT also irreversibly changed into β–NAT. we had also observed same as their observations. In polar night, because of the tempereture of stratospheric airmass is not constant as reported by Adriani et al., (1992), annealing will take place and thereafter solid phase PSCs may changed of its phase. The goal of the direction of phase transformation of nitric acid / water amorphas solid is β–NAT, so it suggested that β–NAT may be the most pronunced phase in later period of polar winter.

In H2SO4 / HNO3 / H2O ternary solution, n–π* absopption of nitric acid hydrate ion was affected by H2SO4 contents. It means hydration of nitric acid affected by existence of sulfuric acid. This effect may affect to the chemistry inside of stratospheric aerozols.

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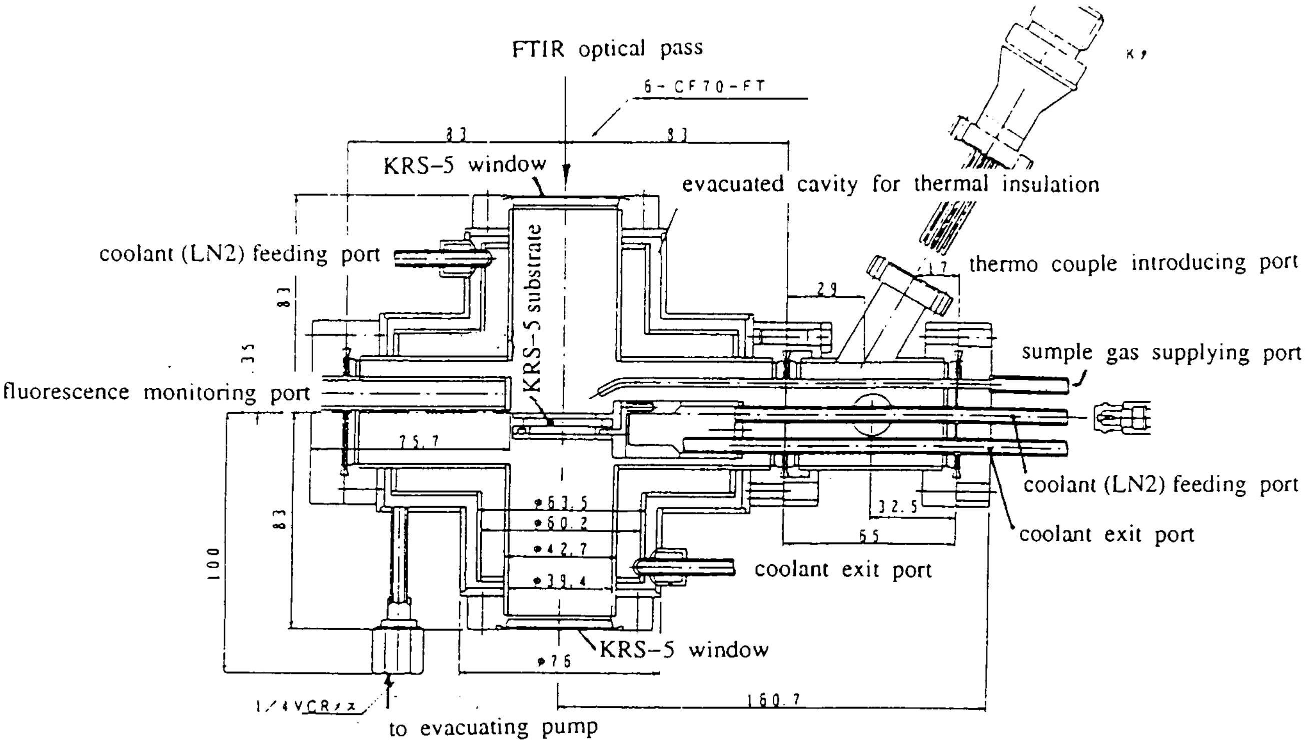

Fig. 1 Schematic of Stratospheric aerosol testing main chamber

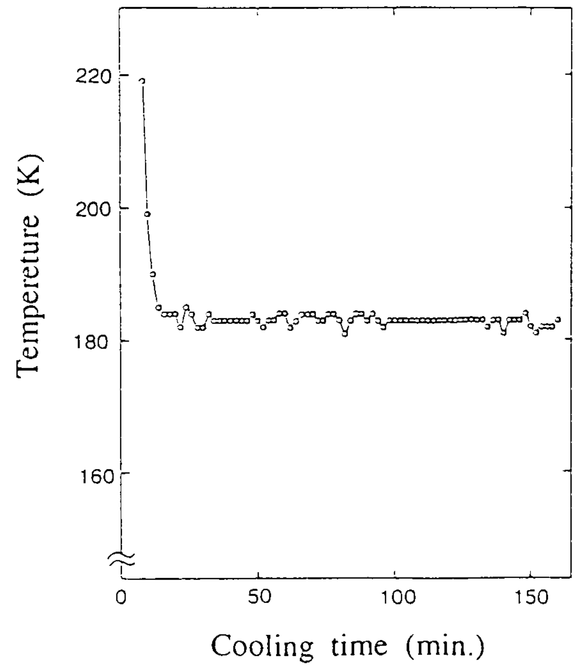

Fig. 2 Cooling test at 183K

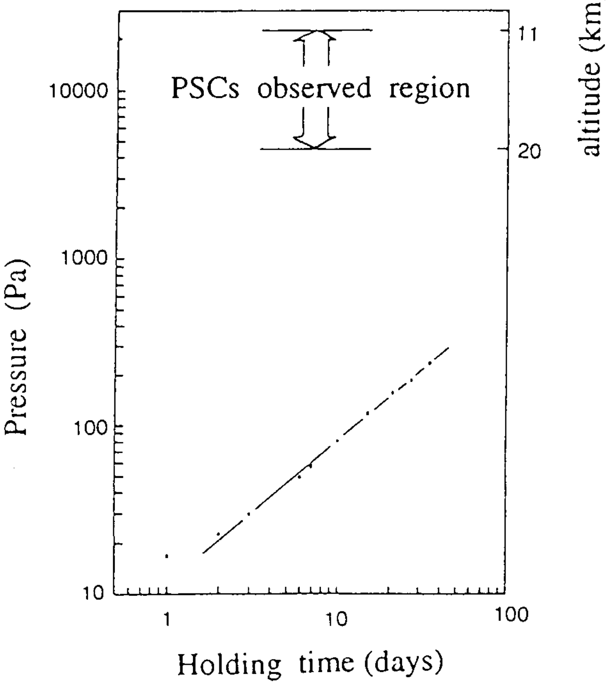

Fig. 3 Gas pressure stability of chamber

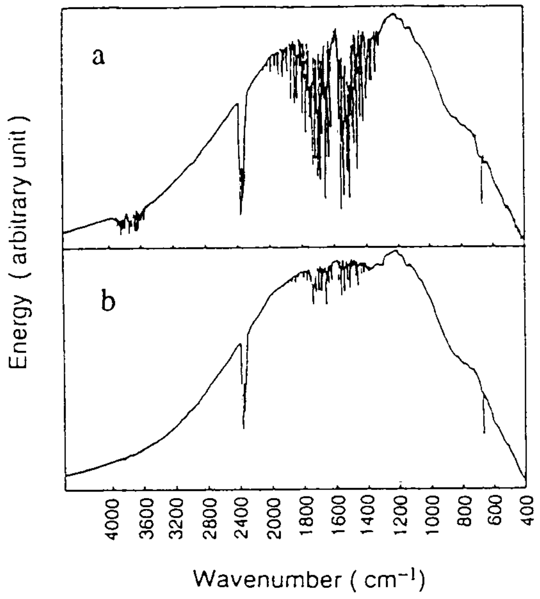

Fig. 4 Purging property of FTIR optical passway by N2 gas
a : without purging
b : with purging

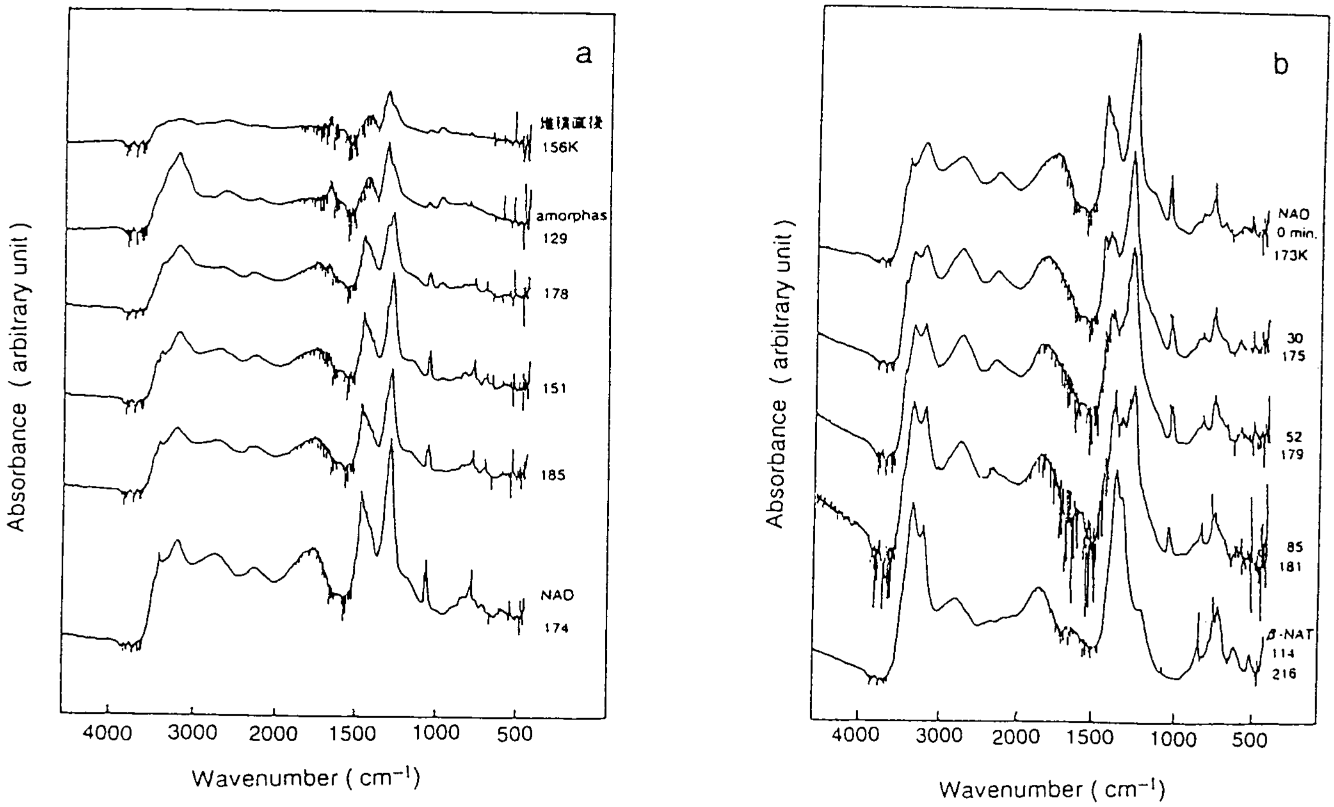

Fig. 5 FTIR absorption spectra of depositted film from nitric acid and water vapour
a : a-NAD → NAD b : NAD → β-NAT

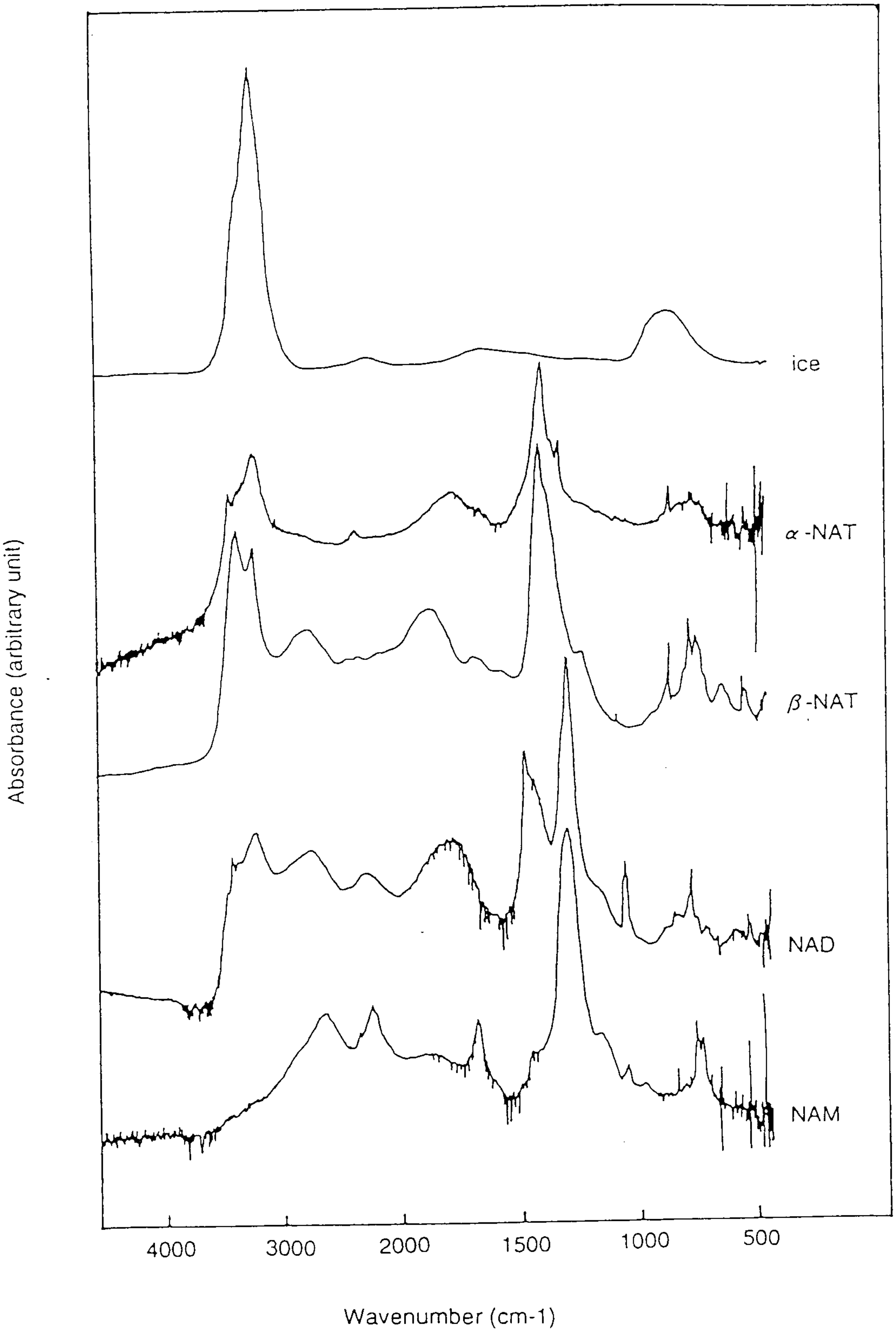

Fig. 6 FTIR absorption spectra of ice and nitric acid hydrate

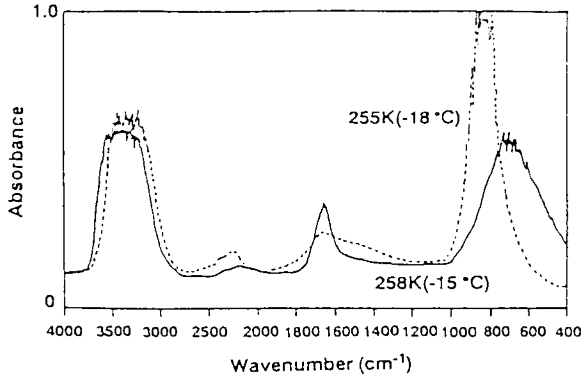

Fig. 7 IR absorption spectra of pure water film during cooling

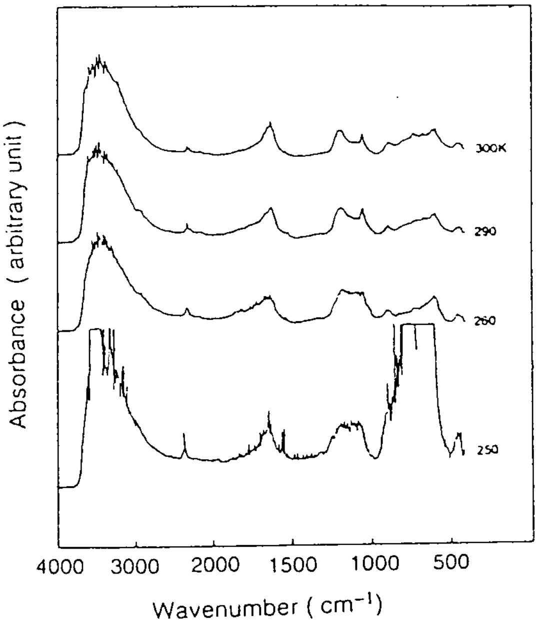

Fig. 8 IR absorption spectra of 1 wt % nitric acid solution during cooling

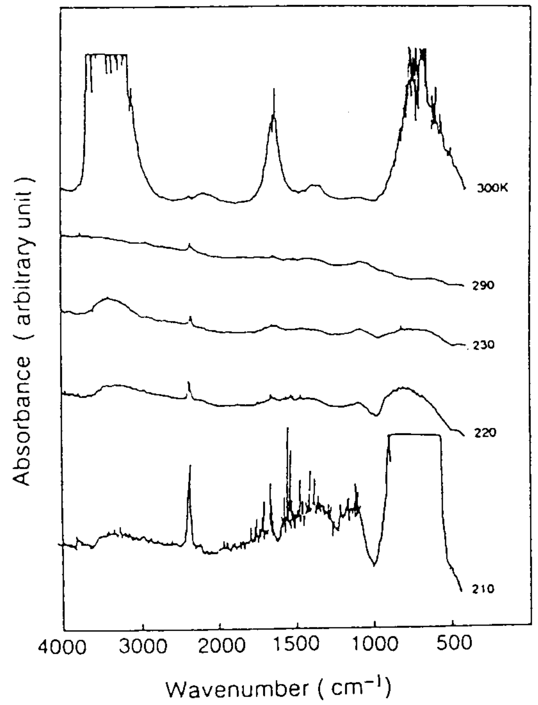

Fig. 9 IR absorption spectra of 10 wt % sulfuric acid solution during cooling

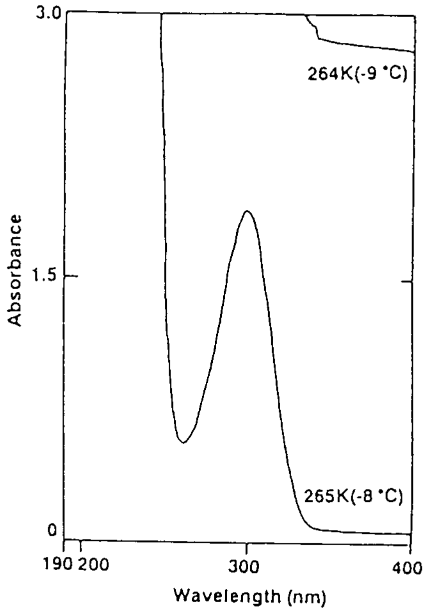

Fig. 10 UV absroption spectra of freezing of 1 wt % nitric acid solution

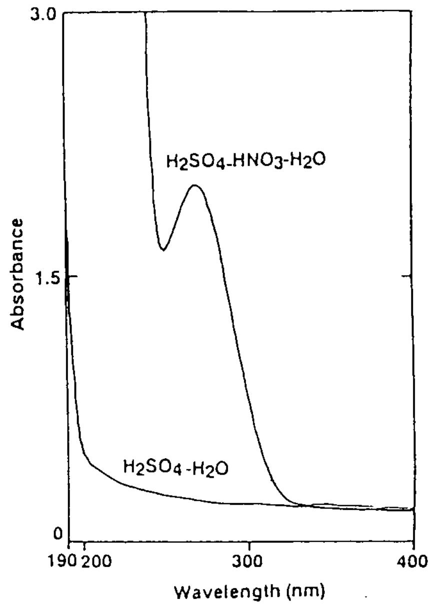

Fig. 11 UV absorption spectra of 10 wt % sulfuric acid solution and H2SO4/HNO3/H2O ternary solution (263K)