A-1.5.2 Research on Characterization of Polar Stratospheric Clouds (PSCs) and their Heterogeneous Interaction with Halogen Reservoir Molecules

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Abstract

We have produced modeled polar stratospheric clouds (PSCs) film that give same infrared spectrum with observed type I PSCs in polar stratosphere (Kinne et al., 1989). The film was characterized as β-type nitric acid trihydrate (β-NAT) measured by optically transparent configuration of FTIR. The same film gave in-situ observed spectrum when it was configured to reflection measurement. As Kramers - Kronig integration of this spectra gave transmittance spectra of β-NAT, it was concluded that reflection spectrum of the film include mainly surface reflection of β-NAT crystals. In spite of reflection spectra of NAT and ice was resembled each other sometimes, we could distinguish them by using Kramers - Kronig integration of spectra.

Key Words Polar Stratospheric Clouds (PSCs), FTIR, Reflection Spectrum, NAT

1. Introduction

As polar stratospheric clouds (PSCs) are known to be important for depletion of stratospheric ozone in wintertime by offering surface for heterogeneous activation of chlorine reservoir molecules, their composition and phase are not exactly determined, especially the case of type I PSCs. They are classified into type I a and type I b: the former is believed as solid particles presumably nitric acid trihydrate (NAT), the latter is believed as aqueous solution which containing nitric acid and sulfuric acid. Although formation and evolution of type I b PSCs are well defined by numerical model that including microphysical and thermodynamical processes (e.g., Carslaw et al., 1995), characterization of type I a PSCs are still undefined. Using infrared spectroscopic data, Toon and Tolbert (1995) was denyed existence of NAT in type I PSCs. However, results from lider observations and model calculations suggest strongly of existence of NAT PSCs (Carslaw et al., 1999). A large part of remote sensed PSCs data must be exist as infrared spectra because of large number of infrared sensors have been operated in these years. If we could retrieve the components and phase of PSCs from these spectra data, it may bring us fruitful result because we already have a lot of spectroscopic data of candidates of PSCs (e.g., Middlebrook et al., 1994), then we can compare and determine observed PSCs. It was difficult, however, to get some information of PSCs from directly observed infrared spectra. To direct this problem, we used an empirical approach that is laboratory experiment which only measure infrared spectra of PSCs candidates film composed nitric acid and water (ice).

2. Research Objective and method

Objective of our research is to retrieve the chemical characteristics of PSCs from remote sensed data such as ADEOS/ILAS infrared solar occultation spectral data. To achieve this goal, at first, we tried to reproduce the infrared spectra of type I PSCs which observed at polar stratosphere in winter to early spring season that is considered most accurate and typical one. The spectra that we selected was Kinne et al.(1989) measured one which was obtained using solar occultation technique with high resolution (0.020 cm^{-1}) FTIR installed on DC-8 aeroplane, at southern polar stratosphere in September 1987 during NASA's AAOE project. This spectrum was obtained from small sized (~0.5 μ m) type I PSCs. Then, we tried to reproduce their spectrum in our laboratory. Thereafter, the film was characterized using infrared spectroscopy of its composition and phase that has same optical properties with observed and selected type I PSCs.

Because of observed infrared spectra of type I PSCs is optically much flat than ice (Kinne et al., 1989), these spectra assigned to be concentrated nitric acid aqueous solutions which is also optically much flat than ice. More recently, Toon and Tolbert (1995) assigned these spectra to much diluted nitric acid aqueous solutions using their measured optical constants (Toon et al., 1994).

We noticed that these optically flat spectra might be produced from multiple scattering condition, for example, the case for reflection with large angle. We had been faced large spectral modulation of ice film which poses large amount of red-shift and broadening of OH stretching peak in its FTIR spectrum when we used such optical configuration. We noticed also, this case would be represents a set of PSCs aerosols by rough surface of modeled PSCs film. Confirmation of this expectation with theoretically is expected to be too difficult to solve, then we decided to perform this in experimentally and empirically. We have been measured ice and nitric acid containing films using high angled reflection optical configuration.

3. Experimental section

While assignment of PSCs candidate using film transmittance optical configuration is easy, however, assignment of infrared spectra of high angled reflection measurement expected to be difficult, infrared spectra of single nitric acid / ice film were measured using both of optical configurations by switching each other. A schematic of the apparatus used is shown in Fig.1. The apparatus consists of low pressure chamber, condensation substrate and Fourier transformation infrared (FTIR) spectrometer (Nihon-bunko, FT/200). The low pressure chamber which equipped with cold cathode and Baratron gauges, KRS-5 (talium iodide and bromide) windows for infrared transmission through the chamber and sample gas inlet, is cooled to polar stratospheric temperature (~190K) with gas produced from liquid nitrogen through it inner jacket.

The condensation substrate made of KRS-5 (30mm: diameter, 3mm: thickness) equipped with K-type thermocouple for measuring temperature is supported and cooled with stainless steel tube (3mm o.d.) which inside through cold gas produced from liquid nitrogen. The tube is supported by chamber vertically to the FTIR optical path through the chamber. When we rotate the tube, the condensation substrate rotates to the FTIR optical path. Modeled PSCs film was prepared by condensation of nitric acid and water vapor onto the cooled substrate. Both of gases were introduced through the sample gas inlet made of stainless steele tube (3mm o.d.) which tip is located near the substrate about 30mm.

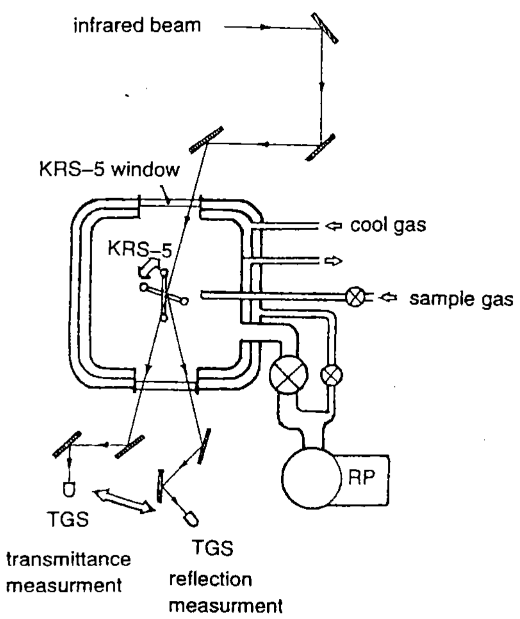

Fig.1. Schematic of the experimental apparatus.

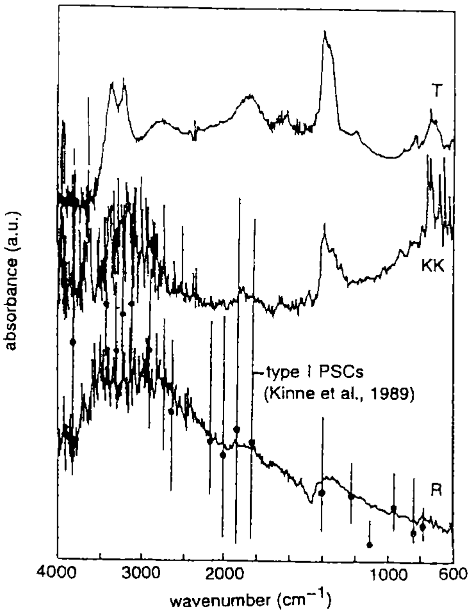

Fig.2. Transmittance (T), reflection (R) and Kramers-Kronig integrated (KK) spectra of β-NAT film.

The film was characterized using FTIR spectroscopy. The infrared beam of FTIR spectrometer was introduced to the chamber through one of the KRS-5 window, then transmitted through film and KRS-5 substrate or reflected at surface or boundary of film and substrate. Transmitted or reflected beam went out of the chamber through another KRS-5 window and reach to the infrared beam detector (TGS) of the FTIR spectrometer. The angle of incidence to the substrate was selected 84 degree. TGS detector moved to adequate place simultaneously when optical configuration was switched. 25 of interferogram were co-added and converted to infrared spectrum with 2 cm^{-1} resolution. These spectra were recorded and analyzed with IBM compatible personal computer. FTIR spectrometer operating and data analyzing software including Kramers- Kronig integration used in this study were supplied from Nihon-bunko corporation

4. Results

Fig.2 shows that reflection spectrum of β-NAT film almost reproduced the spectrum of type I PSCs which obtained by Kinne et al. (1989) at southern polar stratosphere. Conversion of this spectrum using Kramers-Kronig integration gave a spectrum which resembled to transmittance spectrum of β-NAT film.

Fig.3 shows a time series of spectral change of NAT composition film from condensation to melting. Trace a, b, d, f and i are reflection spectra and remained are transmittance spectra. Left-hand of Fig.3 shows absorbance-indicated spectra. In right-hand of Fig.3, transmittance spectra are shown in transmittance. but reflection spectra are converted spectra using Kramers-Kronig integration. Trace b and c, d and e, f and g, h to j were obtained within 5 min. Except the case of trace h to g, each pair of spectra were obtained in almost same conditions. From comparison of transmittance spectra and spectra reported by Koehler et al.(1992), spectrum c and h are composed mainly of α-NAT, e and g are composed of β-NAT, and j is composed of liquid phase nitric acid aqueous solution. Although reflection spectra are difficult to characterize their composition from their spectral shape, their converted spectra using Kramers-Kronig integration are characterized to NAT except trace a and i, because they are almost corresponding with transmittance spectra. As spectrum a recorded when just after film

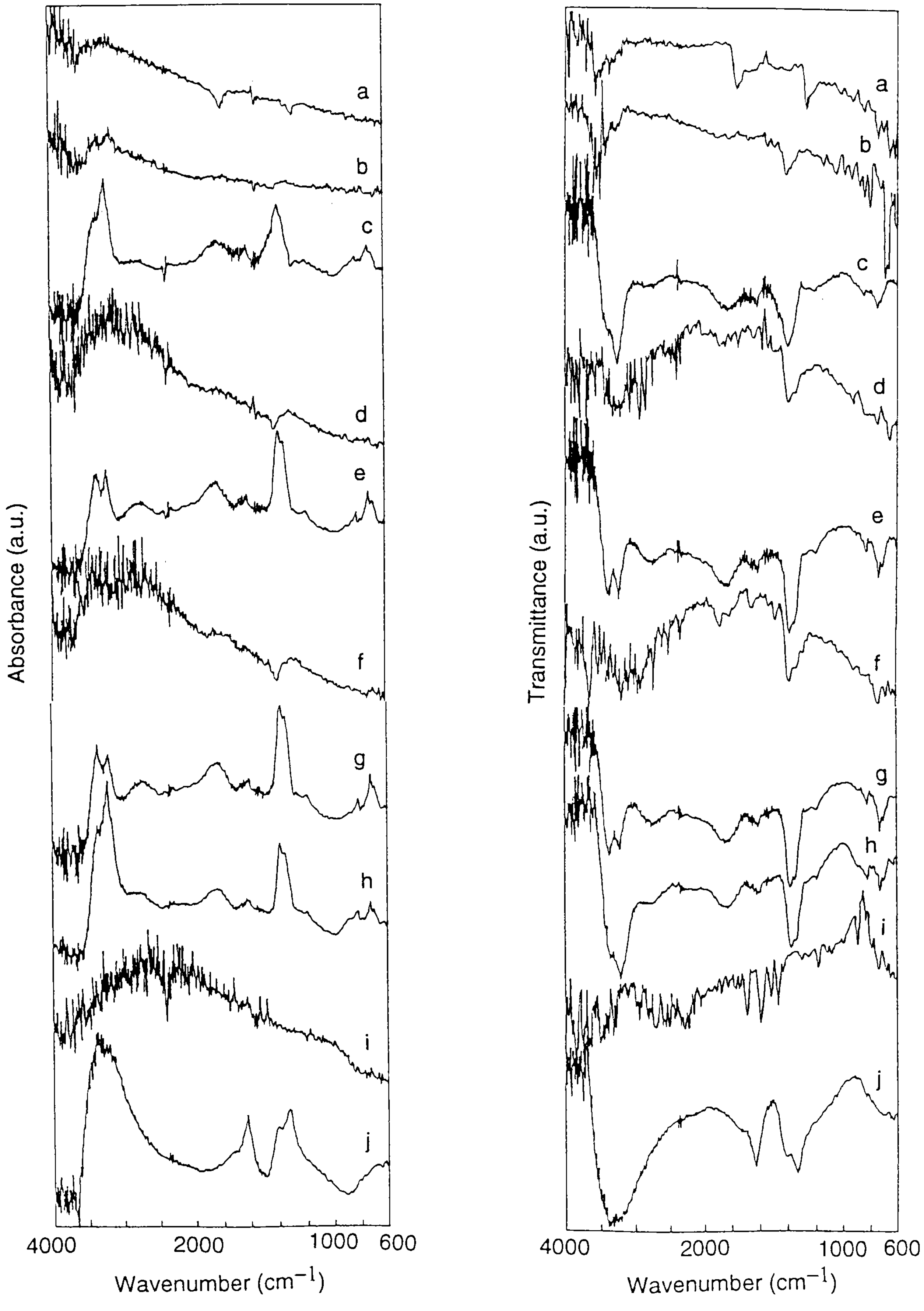

Fig.3. Time series of spectral change of NAT composition film from condensation to melting.

condensation, it is expected to be amorphous phase. The case of trace i, it still difficult to characterize.

When high concentrated nitric acid film is condensed, Kramers-Kronig integrated reflection spectrum of this film shows large absorption peak at ~ 1250 to 1300cm^{-1} where much concentrated phase (e.g., NAM and NAD) shows large absorption. When ice film is condensed, Kramers-Kronig integrated reflection spectrum of this film does not show any absorption in the region where nitric acid and it ion has large absorption. While reflection infrared spectra of films are largely modulated, the results mentioned above show, however, these spectra still retain the information of the film composition.

5. Discussion

As mentioned above, the reflection infrared spectra of NAT film condensed on KRS-5 substrate, that are in accord with type I PSCs spectra obtained in polar stratosphere (Kinne et al, 1989), were converted into transmittance spectra with Kramers-Kronig integration. Because of this integration convert real refractive index into imaginary one, it was suggested that the measured reflection spectra of the film were composed mainly with reflecting beam from surface of NAT crystals. Middlebrook et al.(1994) estimated real refractive index of β-NAT film that value is about 1.51. As we used 84 degree of the angle of incidence, it was estimated that 43% of P-polarized beam and 69% of S-polarized beam was reflected on the surface. It was also estimated that only 10% of P-polarized beam and 3% of S-polarized beam was reflected on the boundary of β-NAT film and KRS-5 substrate. In our experimental configuration, almost of infrared beam reached to the detector are suggested to be reflected one on the surface of the film. If observed infrared spectra of aerosols mainly contain reflection beam at the surface of aerosols, Kramers- Kronig integration would be powerful tool for characterizing aerosols composition.

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