FTIR Spectroscopy of HNO_3 and NO_2 Relevant to Stratospheric Wake Analysis

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Abstract

The Fourier Transform Infrared (FTIR) technique has been employed to measure absolute concentrations of nitric acid (HNO_3) and nitrogen dioxide (NO_2) with 1 cm^{-1} resolution and an absorption pathlength of 4 m under quasi-static and flow conditions at atmospheric pressure and room temperature. Water features seen under quasi-static conditions diminished in intensity under flowing conditions. Nitric acid was observed in the 1660-1760 cm^{-1} range, while nitrogen dioxide was detected both in the 1536-1660 and 1213-1400 cm^{-1} ranges. Concentrations of nitrogen dioxide and nitric acid were determined to be 11.9 and 4.35 parts per million (ppm), respectively, with an uncertainty of 0.2 ppm. Experiments are underway with a 10 m cell to measure the absorption of nitric acid, water, sulfur dioxide, hydrochloric acid and ammonia on various materials such as glass, teflon, stainless steel and aluminum used for implementation of the flow system. Such materials will be used for the measurements of stratospheric trace gases by the Quartz Crystal Microbalance (QCM) and Surface Acoustic Wave (SAW) devices.

Keywords: FTIR; Trace Gases; Stratosphere; Wake; QCM-SAW

Introduction

Emissions from supersonic aircraft include water, carbon dioxide, nitrogen oxides and aerosol particles that participate in atmospheric photochemistry and radiative phenomena.[1] Nitrogen oxides (in the

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form of NO and NO_2) and nitric acid (HNO_3) are present in significant nonequilibrium levels at the exit plane of the engine nozzle.[2]

The Fourier Transform Infrared (FT-IR) spectrometer fingerprints the identifiable chemical species and thereby provides a signature of the molecule. The spectra are recorded by either of two methods: static sample or the constant flow method. Intensities of prominent FTIR spectral features are measured and compared to determine the concentration of each sample (e.g. HNO_3 and NO_2) based on the spectral line intensity. Concentration estimates using this technique have been used for various samples of nitric acid. However, since nitric acid and water adsorb on the walls of the glass cell, their concentrations must be determined by a flow system.

Experimental

An FTIR spectrometer was used for recording the spectra in conjunction with a 4 m pathlength multipass absorption cell employing a flow system that used 100 cc/min of atmospheric air. Initially, zero air was used in the flow system to remove impurities that may be absorbed on the cell walls, such as water (H_2O), ammonia (NH_3), hydrochloric acid (HCl) and sulfur dioxide (SO_2). A given sample of NO_2 contains about 20 % of HNO_3 as impurity, because of the reaction of NO_2 with H_2O on the walls of the lecture bottle used for storing the sample. The FTIR spectra were recorded with a resolution of 1 cm^{-1} and a total of 50-100 scans were needed with the 4 m cell, whereas 1000 scans were required for the 20 cm pathlength cell to achieve comparable resolution.

The flow technique for recording FTIR spectra is being implemented using a 10-m cell, which would increase the sensitivity of the measurements. Such flow measurements will allow one to determine small concentrations (at parts per million level) of reactive species such as HNO_3, H_2O, NH_3 and SO_2.

Results

The HNO_3 feature was observed in the spectral range 1660-1760 cm^{-1}, while the NO_2 transitions were seen both in the 1536-1660 cm^{-1} and the 1213-1400 cm^{-1} ranges. The H_2O features were seen over the entire region 1213-1845 cm^{-1} in the quasi-static mode as shown in Fig. 1. These H_2O spectral lines were substantially diminished in intensity when a flow system was used as illustrated in Fig. 2. The HNO_3 transition around 1700 cm^{-1} showed a characteristic Q-branch appearance, and NO_2 around 1330 cm^{-1} also exhibited a prominent Q-branch. The concentrations determined by the FTIR spectrometer using the 4 m cell were 11.9 ± 0.2 ppm for NO_2 and 4.35 ± 0.2 ppm for HNO_3. Oscillator strength considerations were used for determination of these FTIR concentrations of HNO_3 and NO_2. These results were confirmed by the chemiluminescent detection (CD) technique.[3] For example, the CD value for NO_2 was 11.5 ± 0.2 ppm. Nylon can be used to remove HNO_3 preferentially from the mixture of NO_2 and HNO_3 using the CD technique, so that precise concentrations of both species can be obtained.

References

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Acknowledgment

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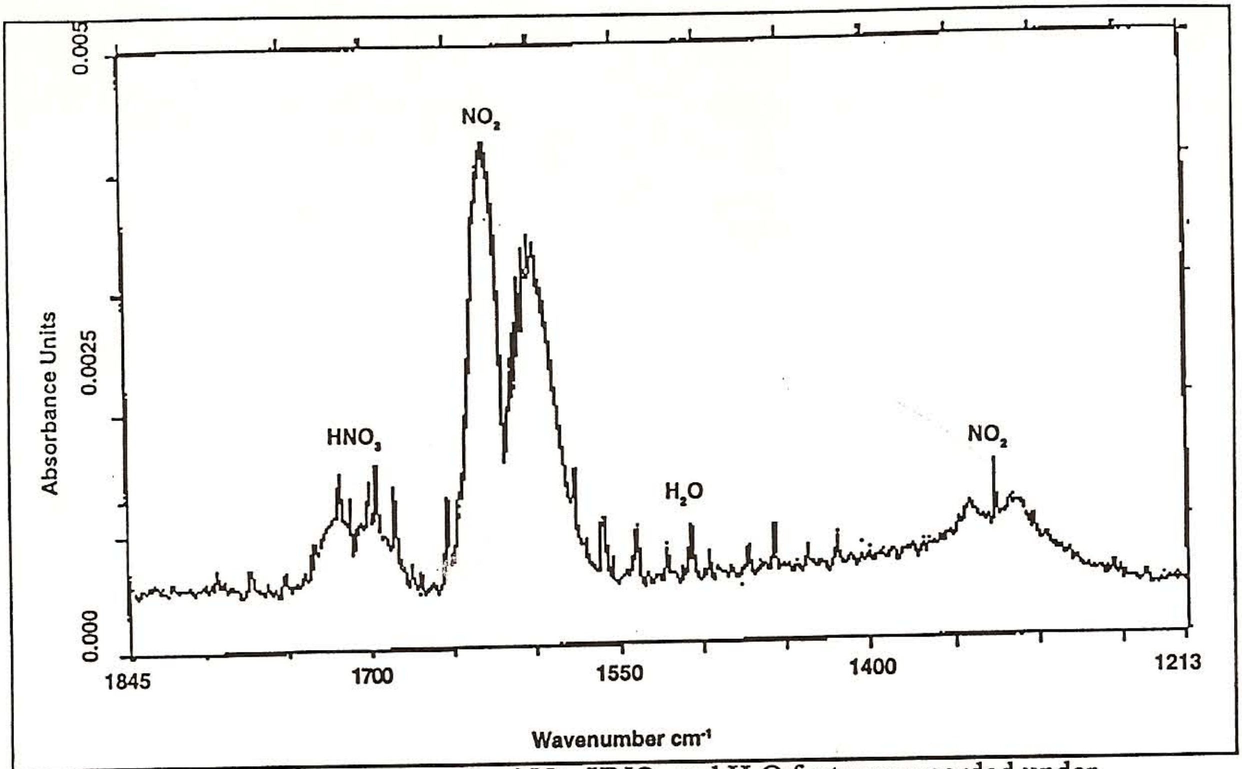

Fig. 1. FTIR spectrum showing NO_2, HNO_3 and H_2O features recorded under quasi-static conditions at 1 cm^{-1} resolution using a 20.7 cm cell and a gas pressure of 747.4 Torr.

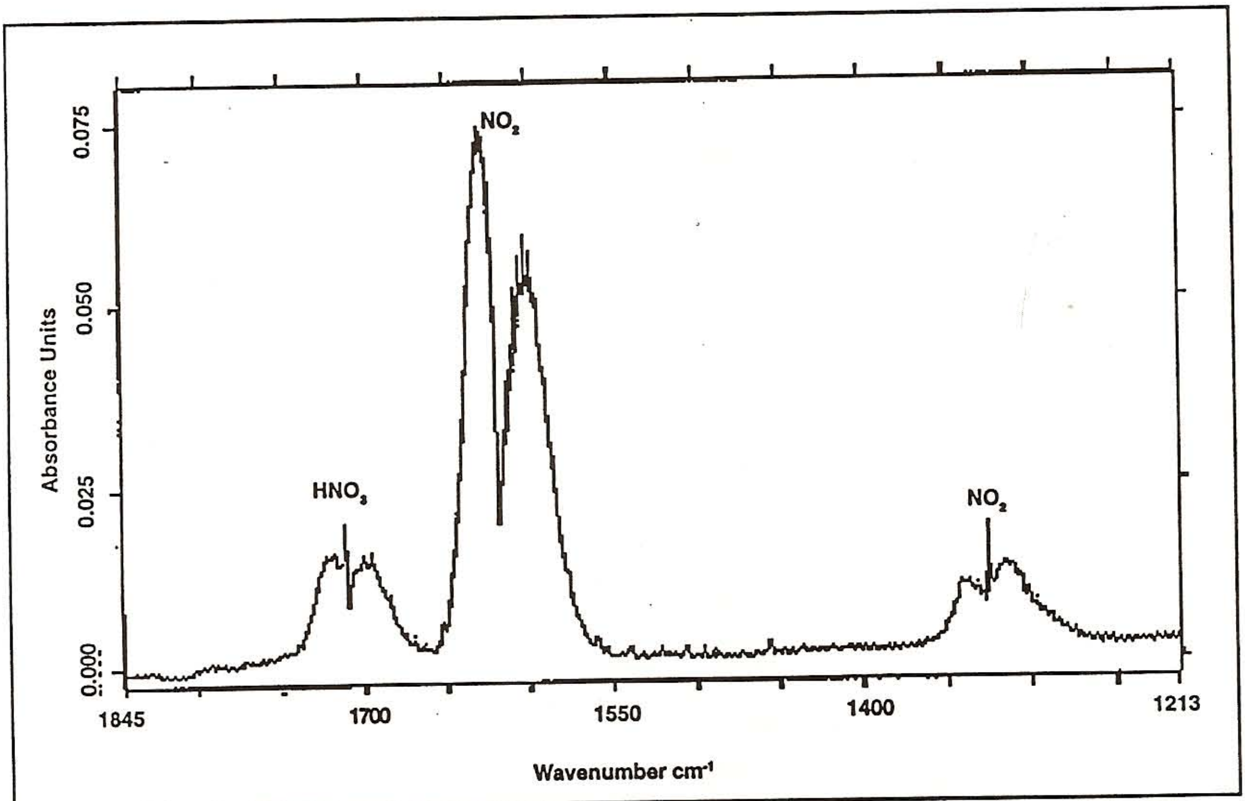

Fig. 2. FTIR spectrum showing HNO_3 and NO_2 features recorded under flow conditions at 1 cm^{-1} resolution using a gas pressure of 751.2 Torr. (Note: the water features go away.)