



Fourier Transform infrared (FT-IR) spectroscopy of trace molecular species of importance for the elucidation of atmospheric phenomena

C. Haridass^a, Abdullahi Aw-Musse^a, P. Misra^{a,*}, J. Jordan^b

^aDepartment of Physics and Astronomy and Center for the Study of Terrestrial and Extraterrestrial Atmospheres (CSTEAs), Howard University, Washington, DC 20059, USA

^bDepartment of Electrical Engineering and Center for the Study of Terrestrial and Extraterrestrial Atmospheres (CSTEAs), Howard University, Washington, DC 20059, USA

Received 1 May 1997; received in revised form 1 October 1997; accepted 1 November 1997

Abstract

Fourier Transform infrared (FT-IR) spectra of nitrogen dioxide, hydrogen chloride and sulfur dioxide have been recorded in the spectral region 400–4000 cm^{-1} with 1–4 cm^{-1} resolution under quasi-static and flow-through conditions through tubings of aluminum, copper, stainless-steel and Teflon. Qualitative and quantitative spectral changes in the FT-IR data are discussed in the context of atmospheric phenomena. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: FT-IR; Atmospheric; Spectroscopy; Infrared radiation

1. Introduction

Fourier Transform infrared (FT-IR) spectroscopy is a dynamical instrumentation technique that is useful for examination of various forms of matter. When a sample is analyzed using infrared radiation, the FT-IR spectra provide information about the vibrational and rotational energies of a molecule. The infrared radiation is absorbed at specific frequencies characteristic of the molecular species, whereby the FT-IR spectrum is a true signature of the molecule.

* Corresponding author. Tel.: +1-202-806-4913; fax: +1-202-806-4429.

E-mail address: pmisra@fac.howard.edu (P. Misra).

Knowing the radiation intensity as a function of the infrared frequency, one can specify the types of chemical functional groups (for example, O–H, COO, C–H, N–H) present in a particular molecular species and also obtain quantitative information, such as the concentration of a molecule in a given sample. A detailed analysis of the rotation–vibration spectrum allows the determination of molecular constants and the temperature of the gas sample used in recording the FT-IR data.

Nitrogen dioxide (NO₂) [1,2], hydrogen chloride (HCl) [2] and sulfur dioxide (SO₂) [2], are known pollutants in the atmosphere. Nitrogen dioxide is found in emissions from aircraft and is a participant in significant atmospheric photochemistry. Hydrogen chloride is a pollutant that also participates in photochemical air pollution. Sulfur dioxide is a known toxin in the atmosphere that is emitted from volcanoes and power plants. Summary of the importance of molecules like NO₂, HCl and SO₂ is given in detail in Ref. [2] and references cited therein. A clearer understanding of these species and the roles these chemicals play in the combustion chain may also lead to the development of improved and efficient organic fuels, in addition to a better understanding of atmospheric phenomena.

Fourier Transform infrared (FT-IR) spectroscopy is a particularly useful analytical technique because of its versatility [3]. Spectra can be obtained of samples in all three states of matter, and in most cases nondestructively. Its distinct advantage over other forms of spectral data acquisition is that it has the ability to look at all the wavelengths of a spectral region simultaneously, rather than one wavelength at a time. Such an approach saves time dramatically and utilizes light more efficiently. In the present work, we report the vibrational and rotational spectra of atmospherically significant molecules, namely NO₂, HCl and SO₂, in the gas phase, which were recorded when these gases were passed through tubes made of different materials, such as aluminum, copper, stainless-steel and Teflon, using a Nicolet Magna-IR 550 Fourier Transform infrared spectrometer. The objective of the present paper is to identify and characterize various tubing materials with respect to their absorption features, so that specific tubing–gas combinations may be determined for designing platforms for airborne atmospheric measurements, and also for quartz crystal microbalance/surface acoustic wave (QCM/SAW) investigations pertaining to measurements of concentrations of trace molecular species in the atmosphere.

2. Experimental

2.1. Sample preparation of the experimental gases NO₂, HCl and SO₂

- NO₂: 15.2 psi of nitrogen dioxide (NO₂) gradually flowed in an evacuated gas cylinder. It was later filled with 960.5 psi of dry nitrogen (N₂) to obtain a sample of 1.58% nitrogen dioxide in the mixture.
- HCl: 529.0 ppm of hydrogen chloride (HCl) was commercially obtained from Scott Specialty Gases, Plumsteadville, PA. This gas was premixed with dry nitrogen (N₂).

- SO₂: 484.0 ppm of sulfur dioxide (SO₂) was commercially obtained from Scott Specialty Gases, Plumsteadville, PA. This gas was premixed with air.

2.2. Description of the FT-IR spectrometer equipped with an absorption cell of 10-m path length

The infrared spectra were recorded using a Nicolet Magna-IR 550 Fourier Transform infrared spectrometer illustrated in Fig. 1. A schematic representation of the spectrometer setup is shown in Fig. 2. It consists of a globar IR source (S) from which the infrared beam enters the interferometer (IF) via mirror (M₁). The interferometer is a Michelson interferometer consisting of four arms. The first arm contains a source of infrared light, the second arm is equipped with a fixed mirror (FM), the third arm contains a moving mirror (MM) and the fourth arm is open. A beam splitter (BS), designed to transmit one half of the radiation that impinges upon it, and reflect the other half of the light, is fixed at the intersection of the four arms. Such positioning of the beam splitter allows the light transmitted by the beam splitter to strike the fixed mirror and the moving mirror. These two light beams recombine at the beam splitter (BS) after being reflected from the mirrors (MM and FM). The recombined beam then exits the interferometer to interact with the sample, which is kept in the sample compartment (SC) and subsequently reaches the detector (D) after being reflected by the mirror (M₂). Every commercial FT-IR instrument is equipped with a He-Ne laser that has a twofold purpose. First, the laser acts as an internal wavenumber standard. All infrared wavenumbers are

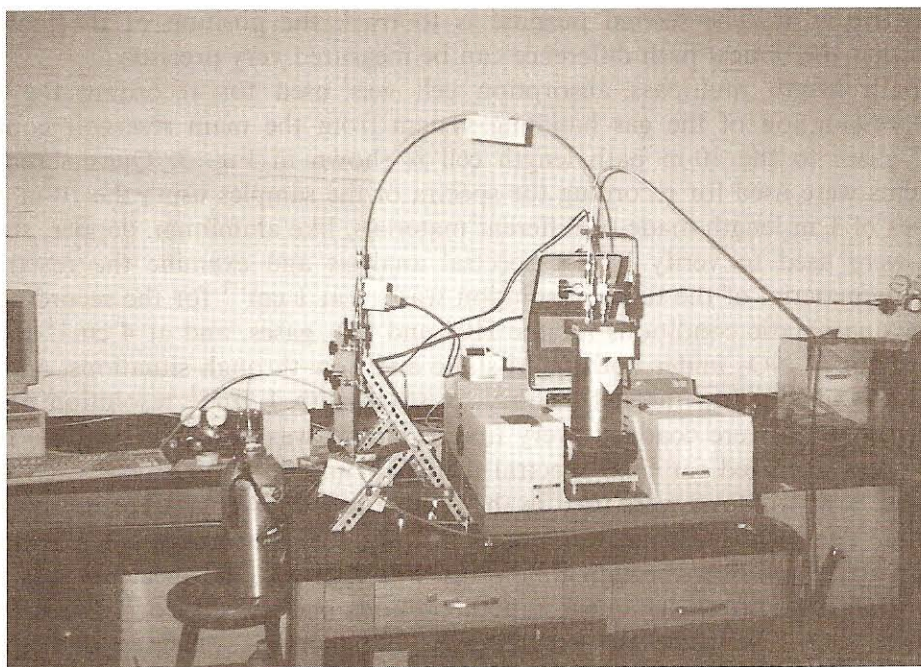


Fig. 1. Nicolet Magna-IR 550 Fourier Transform infrared spectrometer with a 10-m path length multipass gas cell.

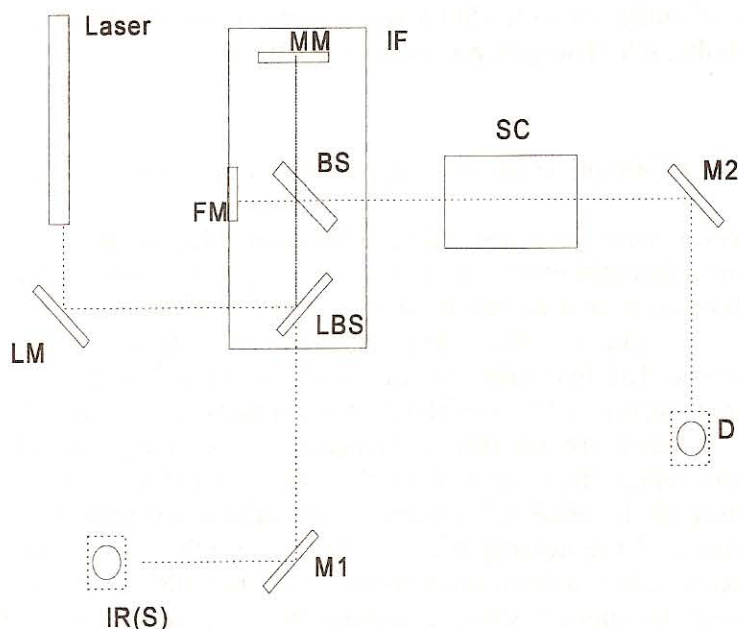


Fig. 2. Schematic representation of the FT-IR spectrometer layout. IR(S) - Infrared Source; LM, M1, M2 - Mirrors; LBS, BS - Beam Splitters; SC - Sample Compartment/cell; MM = Moving Mirror; FM - Fixed Mirror; IF - Michelson Interferometer; D - Mid-IR Detector.

measured relative to it. The second purpose is to track the position of the moving mirror accurately so that the optical path difference can be measured very precisely.

A 10-m path length multipass absorption cell was used for recording the spectra. A schematic representation of the gas handling system from the main reservoir containing the experimental gases to the 10-m path length cell is shown in Fig. 3. Quasi-static and flow-through systems were used for recording the spectra of the samples using the 10-m path length gas cell. Tubes of 1 m length made of different materials, like aluminum, copper, stainless-steel and Teflon, were used to verify FT-IR spectral analysis and examine the reactivity of the sample with the material of the tube. Resolution was set at 1 cm^{-1} for the recording of FT-IR spectra under quasi-static conditions for the HCl and SO_2 gases, and at 4 cm^{-1} for recording the FT-IR spectra of NO_2 under both quasi-static and flow-through situations, and at 4 cm^{-1} for HCl and SO_2 under flow-through. Thirty-six scans with 1 cm^{-1} resolution and 32 scans with 4 cm^{-1} resolution were coadded every time a sample was examined and the results were superimposed and averaged for final spectral display. Time taken to record each spectra was less than 5 min. KBr windows were used in the sample cells for better transmission in the mid-infrared region. The NO_2 spectrum was obtained when the pressure in the cell was 200 Torr for both quasi-static and flow-through conditions. For HCl gas, the spectrum was recorded at a gas pressure of 100 Torr under quasi-static conditions and at 200 Torr under flow-through conditions. The SO_2 spectrum was recorded at 200 Torr of pressure under quasi-static condition and at 80 Torr under flow-through conditions. Spectra were observed for SO_2 in the mid-infrared range $4000\text{--}400\text{ cm}^{-1}$. Characteristics features were obtained for NO_2 in the

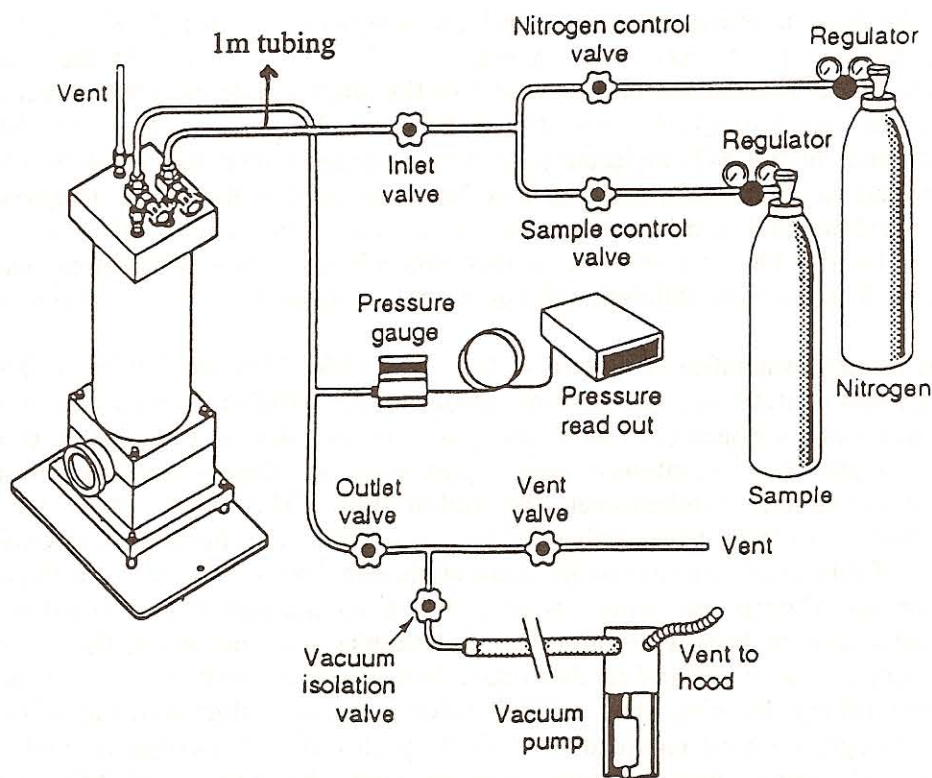


Fig. 3. A schematic representation of the gas handling system from the main reservoir of the experimental gas to the 10-m path length gas cell.

spectral range $1850\text{--}1230\text{ cm}^{-1}$. For hydrogen chloride, a range $3100\text{--}2600\text{ cm}^{-1}$ was useful, and for sulfur dioxide the range was $1425\text{--}400\text{ cm}^{-1}$. The above chosen wavenumber ranges provided signature FT-IR plots characteristic of each molecular species, and obeying the Beer-Lambert law: $I = I_0 \exp(-\sigma_0 Nl)$, where σ_0 is absorption cross-section, N the molecular density and l the absorption path length. The absorbance of each line was then given by $A = \ln(I_0/I)$.

3. Results and discussion

3.1. FT-IR spectral analysis of nitrogen dioxide

The nitrogen dioxide molecule is of great importance to the quantum theory of molecular structure, since it is unique in having an odd electron among the stable triatomic molecules [4]. The determination of the structure and energy levels of NO_2 from its spectrum would considerably increase the quantitative information about molecular orbitals. The NO_2 molecule is an asymmetric top with C_{2v} symmetry [4]. The NO_2 vibration-rotation absorption spectrum consists of A- and B-type bands. In the A-type bands, the oscillating dipole moment lies along

the axis of the least moment of inertia, and the selection rules for J , K_{-1} and K_1 [5] are $\Delta J = 0, \pm 1, J = 0 \leftrightarrow J = 0$; $\Delta K_{-1} = 0, \pm 2, \pm 4, \dots$; $\Delta K_1 = \pm 1, \pm 3, \dots$. In the type B bands, the oscillating dipole moment lies along the axis of the intermediate moment of inertia, and the selection rules are $\Delta J = 0, \pm 1, J = 0 \leftrightarrow J = 0$; $\Delta K_{-1} = \pm 1, \pm 3, \dots$; $\Delta K_1 = \pm 1, \pm 3, \dots$. The fundamental bands of the NO_2 molecule have been recorded under high resolution and precise band centers and rovibrational constants have been obtained in the infrared region [6–13]. A number of overtone and combination bands have also been studied with high resolution spectrometers [14–19]. The present work on this molecule is to study its features, when this gas is subjected to flow through different tubings made of aluminum, copper, stainless-steel and Teflon.

The Fourier transform infrared spectra in the range 1850–1230 cm^{-1} using 1.58% nitrogen dioxide (NO_2) and containing trace amounts of nitric acid (HNO_3), formed due to its reaction with water, using dry nitrogen (N_2) as carrier gas were recorded at a resolution of 4 cm^{-1} . A gas pressure of 200 Torr maintained under quasi-static conditions was used to record the spectra using aluminum, stainless-steel and Teflon tubes. The intensities of the molecular absorption, along with their wavenumbers under quasi-static conditions, are presented in Table 1. The data in Table 1 indicate that under quasi-static conditions, NO_2 reacts with copper, thus showing poor absorbance intensities, in comparison to aluminum and stainless-steel. The absorbance intensities of NO_2 with aluminum and stainless-steel are about the same. Nitrogen dioxide is a very corrosive gas and tends to have high reactivity with metals. This is evident in case of copper tubing. Stainless-steel is a corrosive protectant, thus showing relatively lower reactivity. Although, we have recorded the FT-IR spectra of NO_2 passing through aluminum, stainless-steel and copper tubes; for illustration purposes, the spectrum of NO_2 recorded at a resolution of 4 cm^{-1} when the gas was passed through copper tube is shown in Fig. 4. In this figure, the fundamental bands of NO_2 , a band of HNO_3 and a weak feature around 1500 cm^{-1}

Table 1

FT-IR spectral peaks of 1.58% nitrogen dioxide (NO_2) in N_2 under quasi-static conditions at a gas pressure of 200 Torr using a 10-m path length multipass gas cell

Molecular species	Mode	ν (cm^{-1})	Absorbance ^a		
			Aluminum	Stainless-steel	Copper
HNO_3		1719.0	–	0.0538	0.0296
HNO_3		1719.0	–	0.0538	0.0296
HNO_3		1712.5	–	0.0540	0.0296
HNO_3		1699.6	–	0.0537	0.0305
NO_2	$\nu_3(\text{B}_1)$	1628.8	0.301	0.3150	0.1200
NO_2		1608.3	0.226	0.2240	0.0898
NO_2		1596.4	0.224	0.2370	0.0916
NO_2	$\nu_1(\text{A}_1)$	1339.3	–	0.0422	–
NO_2		1324.9	–	0.0457	–
NO_2		1313.9	–	0.0451	–

^a The uncertainty in the measurement of the absorbance is 0.001.

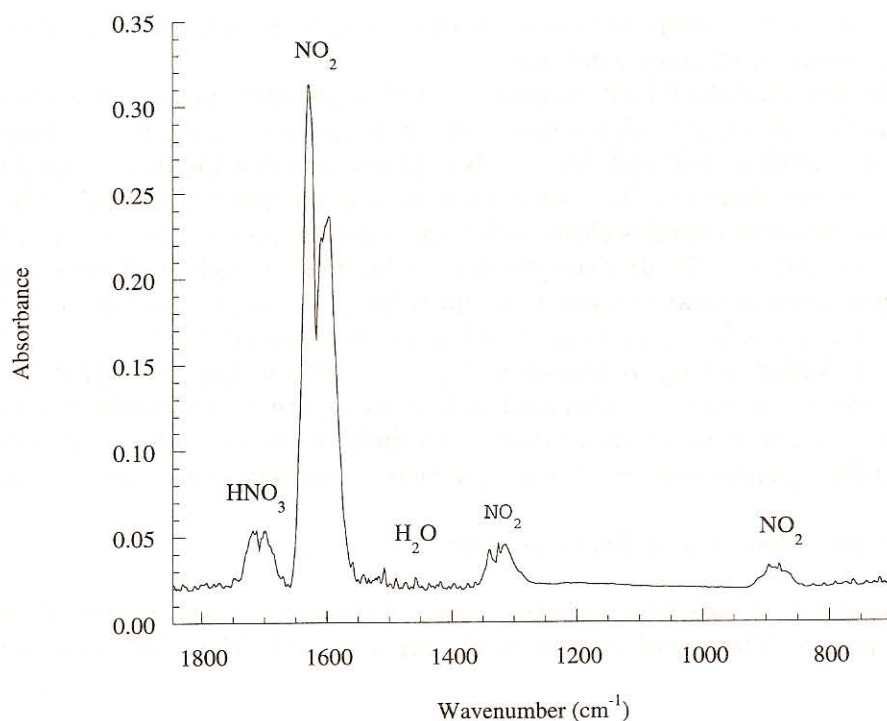


Fig. 4. FT-IR spectrum of 1.58% nitrogen dioxide (NO_2) in N_2 under quasi-static conditions at 4.0cm^{-1} resolution with a gas pressure of 200 Torr when the gas passes through Teflon tube.

Table 2

FT-IR spectral peaks of 1.58% nitrogen dioxide (NO_2) in N_2 under flow-through conditions at a gas pressure of 200 Torr using a 10 m path length multipass gas cell

Molecular Species	Mode	ν (cm^{-1})	Absorbance ^a		
			Aluminum	Stainless-steel	Teflon
HNO_3		1719.0	–	0.0365	0.0296
HNO_3		1712.5	–	0.0385	0.0315
HNO_3		1699.6	–	0.0336	0.0263
NO_2	$u_3(B_1)$	1628.8	0.311	0.3280	0.2750
NO_2		1608.3	0.217	0.2290	0.1920
NO_2		1596.4	0.231	0.2440	0.2030
NO_2	$u_1(A_1)$	1339.3	–	0.0241	0.0192
NO_2		1324.9	–	0.0321	0.0263
NO_2		1313.9	–	0.0301	0.0248

^a The uncertainty in the measurement of the absorbance is 0.001.

due to water vapor, are clearly identified. Water vapor is present because NO_2 tends to be water-retentive under quasi-static conditions.

We have also recorded the FT-IR spectrum of 1.58% nitrogen dioxide (NO_2) in dry nitrogen (N_2) at a resolution of 4 cm^{-1} , with a gas pressure of 200 Torr under flow-through conditions using aluminum, stainless-steel and Teflon tubes, to find whether the flow conditions may have any effect on the absorbance of the molecules with different tubing materials. The absorbance intensities of the molecular species along with their wavenumbers are presented in Table 2. The values of the absorbance in Table 2 suggest that under flow-through conditions, the gas sample seems to be inert when it flows through different tubings. A sample spectrum of 1.58% NO_2 in dry N_2 recorded at a resolution of 4 cm^{-1} , with a gas pressure of 200 Torr, under flow-through conditions using Teflon tubing, is shown in Fig. 5. In this figure, the fundamental bands of NO_2 , and a band of HNO_3 , are identified and labeled. The flow-through method eliminates absorption features due to water vapor (H_2O) and thereby allows improved spectral analysis of important mid-IR signature spectra of atmospherically important trace molecular species.

3.2. FT-IR spectral analysis of hydrogen chloride

In vibration-rotation spectroscopy, transitions between various rotational energy levels associated with two different vibrational levels are observed. The vibrational transitions are

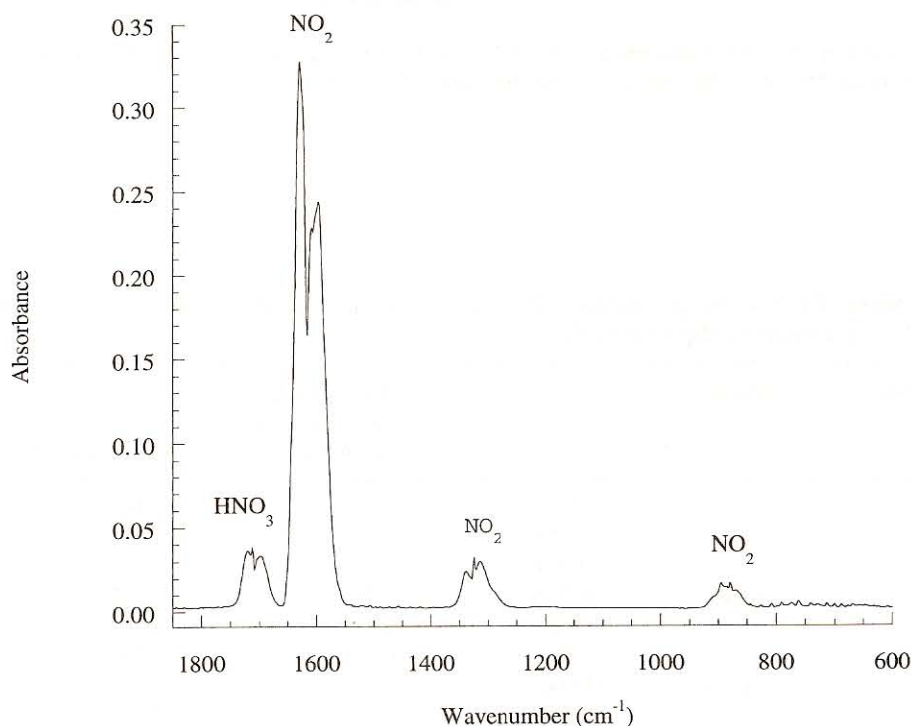


Fig. 5. FT-IR spectrum of 1.58% nitrogen dioxide (NO_2) in N_2 under flow-through conditions at 4.0 cm^{-1} resolution with a gas pressure of 200 Torr when the gas passes through Teflon tubing.

observed when the sample is in any of three possible phases, whereas the rotational transitions are observed primarily in the gas phase at low pressure and usually in an absorption process.

For a diatomic molecule, like HCl, which has no net spin or orbital angular momentum (in the ground electronic state $^1\Sigma^+$), the spectrum contains only P and R branches, according to the selection rules $\Delta J = \pm 1$. The FT-IR spectrum of the fundamental band (1–0) of the diatomic molecule $^1\text{H}^{35}\text{Cl}$ and its isotopomer $^1\text{H}^{37}\text{Cl}$, in the spectral region $3100\text{--}2600\text{ cm}^{-1}$ in dry nitrogen (N_2), recorded at a resolution of 1 cm^{-1} , and with a gas pressure of 100 Torr, under quasi-static conditions is shown in Fig. 6. In a natural isotopic sample, the ^{35}Cl and ^{37}Cl occur with a 3:1 abundance ratio. The absorptions due to $^1\text{H}^{37}\text{Cl}$ are displaced to the low wavenumber side relative to that due to $^1\text{H}^{35}\text{Cl}$ because of the larger reduced mass. The assigned rotational quantum numbers, the wavenumbers of the P and R branch lines, along with the corresponding absorbance, for the four tubes made of aluminum, copper, stainless-steel and Teflon, are given in Table 3. The fundamental bands of HCl and its isotopomer have been studied very exhaustively [20–23]. The main purpose of recording the fundamental band of HCl using a Fourier Transform infrared spectrometer in the present work is to understand the changes in the spectra when the gas flows through tubes made with different materials. Wavenumbers reported in the present work for both R and P branch lines agree with the literature data [23–25] to within about $0.01\text{--}0.08\text{ cm}^{-1}$, for the observed J values. It is clear from Table 3 that absorbances are higher when the gas passes through tubes made of stainless-

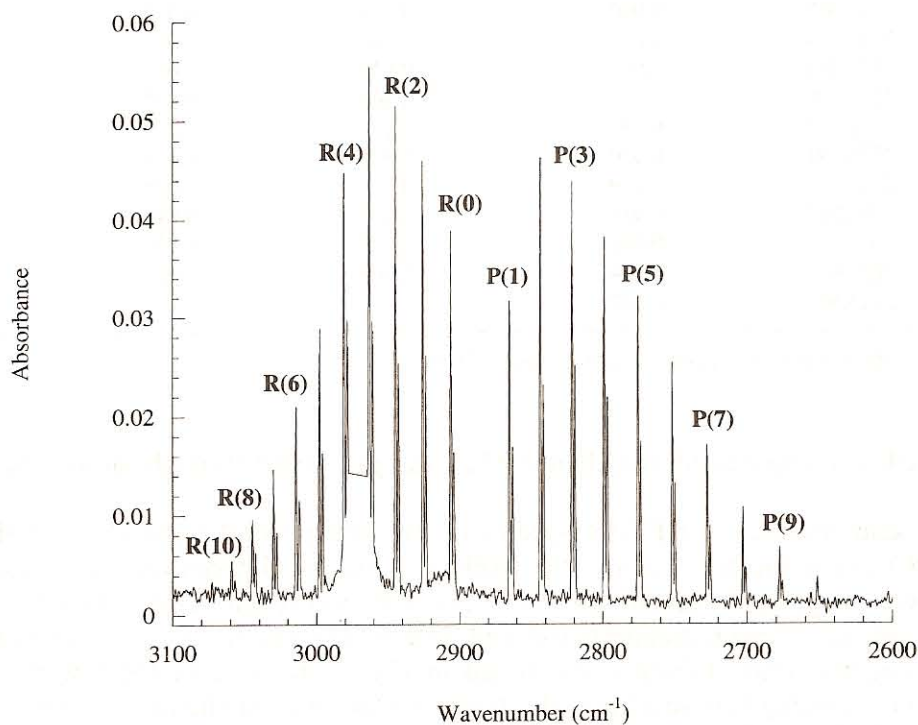


Fig. 6. FT-IR spectrum of hydrogen chloride (HCl) under quasi-static conditions at 1.0 cm^{-1} resolution with a gas pressure of 100 Torr when the gas passes through copper tubing.

Table 3

FT-IR spectral peaks of hydrogen chloride $^1\text{H}^{35}\text{Cl}$ in N_2 under quasi-static conditions at a resolution of 1 cm^{-1} with a gas pressure of 100 Torr using a 10-m path length multipass gas cell

<i>J</i>	$\nu\text{ (cm}^{-1}\text{)}$	Absorbance ^a			
		Aluminum	Copper	Stainless-steel	Teflon
	<i>R(J)</i>				
0	2906.224	0.044	0.039	0.059	0.060
1	2925.898	0.052	0.047	0.072	0.073
2	2944.843	0.058	0.052	0.078	0.078
3	2963.200	0.053	0.056	0.076	0.074
4	2980.953	0.046	0.045	0.064	0.064
5	2997.947	0.033	0.030	0.044	0.045
6	3014.317	0.023	0.021	0.031	0.032
7	3030.064	0.017	0.015	0.021	0.023
8	3045.029	0.010	0.010	0.015	0.015
9	3059.230	0.006	0.006	0.008	0.010
10	3072.773	0.004	0.007	0.005	0.007
11	3085.596	–	–	–	0.006

<i>J</i>	<i>P(J)</i>	Aluminum	Copper	Stainless-steel	Teflon
1	2865.077	0.040	0.034	0.052	0.055
2	2843.574	0.053	0.046	0.071	0.072
3	2821.475	0.052	0.045	0.069	0.070
4	2798.850	0.046	0.040	0.061	0.062
5	2775.673	0.037	0.033	0.050	0.051
6	2751.981	0.029	0.025	0.038	0.039
7	2727.773	0.019	0.017	0.025	0.027
8	2702.937	0.012	0.011	0.016	0.017
9	2677.70	0.008	0.007	0.010	0.012
10	2651.93	0.004	0.004	0.005	0.007
11	2625.67	0.002	–	–	–

^a The uncertainty in the measurement of absorbance is 0.001.

steel and Teflon, compared to absorbance when the gas passes through aluminum and copper tubings.

We have also recorded the FT-IR spectra of the fundamental band (1–0) of the diatomic molecule HCl in the spectral region $3100\text{--}2600\text{ cm}^{-1}$, in dry nitrogen (N_2), at a resolution of 4 cm^{-1} and with a gas pressure of 200 Torr under flow-through conditions using four tubes made of aluminum, copper, stainless-steel and Teflon. The spectrum of the fundamental band obtained using aluminum tubing is illustrated in Fig. 7. Because of the low resolution of 4 cm^{-1} used in recording this spectrum, the fundamental band of the isotopomer $^1\text{H}^{37}\text{Cl}$ is not resolved in this figure. The assigned rotational quantum numbers, the wavenumbers of the P and R branch lines, along with the absorbance, when the gas was passed through aluminum, copper, stainless-steel and Teflon tubes are given in Table 4. The values given in Table 4

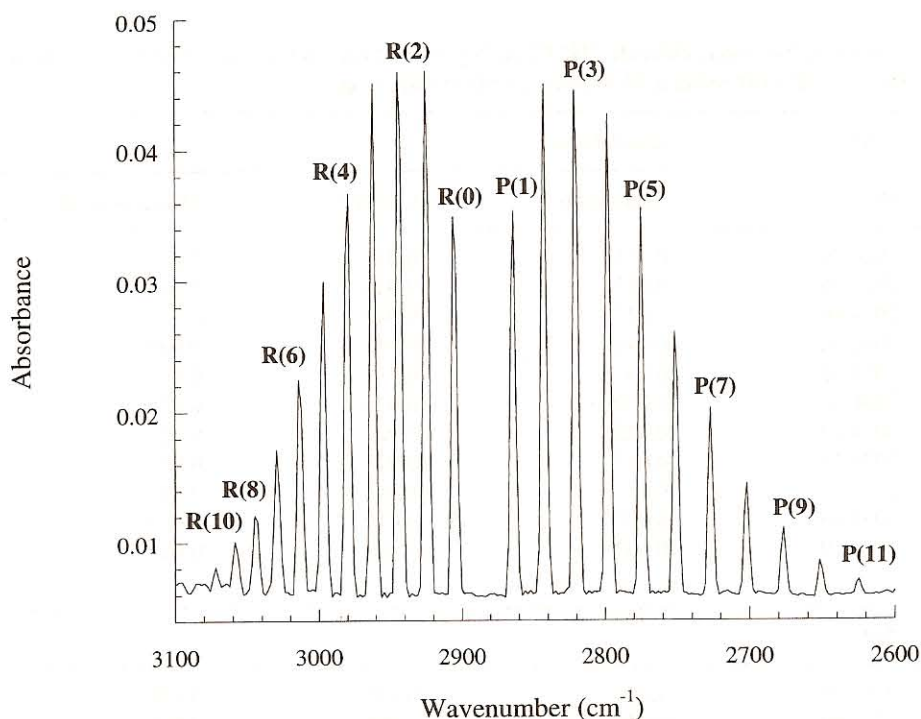


Fig. 7. FT-IR spectrum of hydrogen chloride (HCl) under flow-through conditions at 4.0cm^{-1} resolution with a gas pressure of 200 Torr when the gas passes through Aluminium tubing.

suggest that there is a detectable variation in the measured absorbance for HCl when it is passed through the Teflon tubing.

The accuracy of the observed wavenumbers of the rotational lines of $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ are verified by analyzing the 1–0 band and comparing the molecular constants obtained for the upper and lower states with the values available in the literature [23–25]. A nonlinear least-squares fit was carried out for the observed R and P branch lines for both the upper and lower states along with their band origins. The wavenumbers along with their (obs-cal) differences and the values given in Ref. [23] are given in Table 5 for $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ and the molecular constants are given in Table 6. Rotational constants thus deduced in the present work are found to be in good agreement with the values reported in the literature [23–25]. The rotational temperatures of the $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ gas components in the absorption cell are determined from the R(3) line of Fig. 6 and using the expression $J_{\text{max}} \approx \sqrt{kT/2Bhc} - \frac{1}{2}$ [26] and determined to be 368.0437(95) and 367.4691(88) K, respectively.

3.3. FT-IR spectral analysis of sulfur dioxide

Sulfur dioxide is one of the most important pollutants in the burning of fossil fuels. The amount of SO_2 produced is directly related to the sulfur content of the fuel. In the atmosphere, SO_2 is converted to sulfuric acid and sulfate particles largely responsible for acid rain. Like

Table 4

FT-IR spectral peaks of hydrogen chloride $^1\text{H}^{35}\text{Cl}$ in N_2 under flow-through conditions at a resolution of 4 cm^{-1} with a gas pressure of 200 Torr using a 10-m path length multipass gas cell

J	$\nu\text{ (cm}^{-1}\text{)}$	Absorbance ^a			
		Aluminum	Copper	Stainless-steel	Teflon
	R(J)				
0	2906.20	0.035	0.035	0.030	0.013
1	2925.50	0.047	0.046	0.040	0.017
2	2944.80	0.047	0.046	0.040	0.017
3	2962.20	0.046	0.045	0.039	0.017
4	2979.50	0.037	0.037	0.032	0.014
5	2996.90	0.030	0.030	0.026	0.012
6	3014.20	0.022	0.022	0.020	0.010
7	3029.70	0.017	0.017	0.015	0.009
8	3045.10	0.011	0.012	0.011	0.007
9	3058.60	0.009	0.010	0.009	0.006
10	3072.10	0.007	0.008	0.007	0.006
J	P(J)				
1	2863.80	0.040	0.035	0.030	0.012
2	2842.60	0.046	0.045	0.039	0.016
3	2821.40	0.045	0.044	0.038	0.017
4	2798.20	0.043	0.043	0.037	0.016
5	2775.10	0.036	0.035	0.031	0.014
6	2752.00	0.026	0.026	0.023	0.011
7	2726.90	0.020	0.020	0.017	0.009
8	2701.80	0.014	0.014	0.013	0.007
9	2676.70	0.010	0.011	0.010	0.006
10	2651.70	0.008	0.008	0.005	0.005
11	2624.70	0.006	0.007	0.006	0.005

^a The uncertainty in the measurement of absorbance is 0.001.

nitrogen dioxide, sulfur dioxide is an asymmetric top molecule with C_{2v} symmetry [4]. Its infrared spectrum is very complex. High-resolution microwave and far infrared spectra of SO_2 arising from pure rotational transitions in the ground and excited states have been studied by many investigators [27–34]. Selected individual transitions of the ν_1 and ν_3 vibration–rotation bands of SO_2 have been studied based on the spectra recorded with tunable lasers [35,36]. In the present work, we have recorded the FT-IR spectrum in the spectral range $1425\text{--}400\text{ cm}^{-1}$ of sulfur dioxide (SO_2) in air at a resolution of 1.0 cm^{-1} and with a gas pressure of 200 Torr, under quasi-static conditions, using aluminum, stainless-steel, copper, and Teflon tubings. The spectral features of the fundamental bands ($\nu_1 = 517.75\text{ cm}^{-1}$, $\nu_2 = 1151.65\text{ cm}^{-1}$ and $\nu_3 = 1362.0\text{ cm}^{-1}$) of SO_2 under quasi-static conditions using copper tubing are shown in Fig. 8. In this figure, the fine structure of the fundamental bands is seen clearly. Wavenumbers of the bands and the absorbance values when the gas was passed through tubes made of four different

Table 5

Wavenumbers (in cm^{-1}) of the rotational lines of the fundamental (1–0) band of $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ recorded using the FT-IR spectrometer

<i>J</i>	$^1\text{H}^{35}\text{Cl}$		$^1\text{H}^{37}\text{Cl}$	
	$R_{\text{cc}}(J)^{\text{a}}$	$R_{\text{cc}}(J)^{\text{b}}$	$R_{\text{cc}}(J)^{\text{a}}$	$R_{\text{cc}}(J)^{\text{b}}$
0	2906.224(33)	2906.246352(38)	2904.109(17)	2904.110379(35)
1	2925.898(59)	2925.896078(02)	2923.683(–31)	2923.731539(04)
2	2944.843(–09)	2944.913000(16)	2942.741(35)	2942.721325(05)
3	2963.200(–19)	2963.284896(12)	2961.094(40)	2961.067587(03)
4	2980.953(26)	2980.999803(–14)	2978.676(–70)	2978.758404(04)
5	2997.947(–17)	2998.045986(–37)	2995.774(02)	2995.782022(–25)
6	3014.317(–03)	3014.411893(–69)	3012.099(–21)	3012.126968(–44)
7	3030.064(–82)	3030.086294(–13)	3027.732(–46)	3027.782010(02)
8	3045.029(–89)	3045.057974(05)	3042.684(–51)	3042.735977(06)
9	3059.230(47)	3059.316154(63)	3056.938(–42)	3056.978135(60)
10	3072.773(74)	3072.850059(–00)		

<i>J</i>	$^1\text{H}^{35}\text{Cl}$		$^1\text{H}^{37}\text{Cl}$	
	$P_{\text{cc}}(J)^{\text{a}}$	$P_{\text{cc}}(J)^{\text{b}}$	$P_{\text{cc}}(J)^{\text{a}}$	$P_{\text{cc}}(J)^{\text{b}}$
1	2865.077(36)	2865.097721(–31)	2862.968(–36)	2863.023094(–32)
2	2843.574(10)	2843.624158(25)	2841.605(42)	2841.582218(14)
3	2821.475(–28)	2821.567988(–09)	2819.525(–16)	2819.560056(–07)
4	2798.850(–20)	2798.942287(–13)	2796.910(–33)	2796.969606(–19)
5	2775.673(–06)	2775.760103(–19)	2773.768(–38)	2773.823906(–09)
6	2751.981(37)	2752.034666(16)	2750.090(–30)	2750.136108(13)
7	2727.773(97)	2727.779199(28)	2725.905(01)	2725.919428(21)
8	2702.937(47)	2703.007066(14)	2701.176(02)	2701.187184(11)
9	2677.70 (10)	2677.731754(27)	2675.877(–64)	2675.952865(75)
10	2651.93 (11)	2651.966649(–40)	2650.198(–23)	2650.229711(07)
11	2625.67 (11)	2625.72534 (–13)		

^a Number in parentheses indicates the $(\nu_{\text{obs}} - \nu_{\text{cal}}) \times 10^3$ value in units of cm^{-1} .

^b Number in parantheses indicates the $(\nu_{\text{obs}} - \nu_{\text{cal}}) \times 10^4$ value in units of cm^{-1} [23].

materials aluminum, copper, stainless-steel and Teflon, are presented in Table 7. These values suggest that there is no significant variation in absorption of SO_2 when different tubings made of materials such as aluminum, copper, stainless-steel and Teflon are used. We have recorded the FT-IR spectrum of sulfur dioxide in air in the spectral region $1425\text{--}400\text{ cm}^{-1}$, at a resolution of 4 cm^{-1} , with a gas pressure of 80 Torr under flow-through conditions using aluminum, copper, stainless-steel and Teflon tubings (see for example, Fig. 9). The wavenumbers of the bands and the corresponding absorbances are given in Table 8. Based upon the values presented in this table, it is clear that there is no noticeable variation in absorbance when SO_2 passes through tubes made of different materials under flow-through conditions.

Table 6

Rotational constants^a (in cm^{-1}) of the $\nu = 1$ and 0 levels of the $X^1\Sigma^+$ state of $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ obtained from the non-linear least-squares fit

Molecular constant	$^1\text{H}^{35}\text{Cl}$	$^1\text{H}^{35}\text{Cl}^b$
$\nu_0(1-0)$	2885.921(17)	2885.976036(10)
B_1	10.13614(40)	10.13618163(65)
$D_1 \times 10^4$	5.21372997 ^c	5.213730(94)
$H_1 \times 10^8$	1.60551862 ^c	1.6055(47)
B_0	10.44102(27)	10.44019811(38)
$D_0 \times 10^4$	5.28075888 ^c	5.280759(79)
$H_0 \times 10^8$	1.67366388 ^c	1.6737(51)
Variance of fit (σ)	2.38	
Weighted S.D.	5.2×10^{-2}	9.99×10^{-6}
Molecular constant	$^1\text{H}^{37}\text{Cl}$	$^1\text{H}^{37}\text{Cl}^b$
$\nu_0(1-0)$	2883.851(12)	2883.8700505(79)
B_1	10.12154(35)	10.12118632(56)
$D_1 \times 10^4$	5.19810135 ^c	5.198101(87)
$H_1 \times 10^8$	1.59867096 ^c	1.5987(38)
B_0	10.42472(25)	10.42451511(28)
$D_0 \times 10^4$	5.26486170 ^c	5.264862(59)
$H_0 \times 10^8$	1.66826732	1.6683(39)
Variance of fit (σ)	1.29	
Weighted S.D.	3.8×10^{-2}	7.22×10^{-6}

^a Numbers in parentheses indicate uncertainty in the last digits.

^b Numbers in parentheses indicate uncertainty in the last digits of the rotational constants quoted from Ref. [23].

^c Fixed constant in the least-squares fit.

Table 7

FT-IR spectral peaks of sulfur dioxide (SO_2) in air under quasi-static conditions at a gas pressure of 200 Torr using a 10-m path length multipass gas cell

Mode	ν (cm^{-1})	Absorbance ^a			
		Aluminum	Copper	Stainless-steel	Teflon
$b_1(\text{SO}_2)$	1371.71	0.919	0.927	0.920	0.804
	1360.89	1.180	1.194	1.190	1.038
	1350.97	0.712	0.715	0.710	0.625
$a_1(\text{SO}_2)$	1163.31	0.103	0.103	0.102	0.091
	1132.51	0.102	0.102	0.102	0.091
$a_2(\text{SO}_2)$	533.90	0.129	0.128	0.130	0.111
	503.22	0.119	0.119	0.117	0.105

^a The uncertainty in the measurement of the absorbance is 0.001.

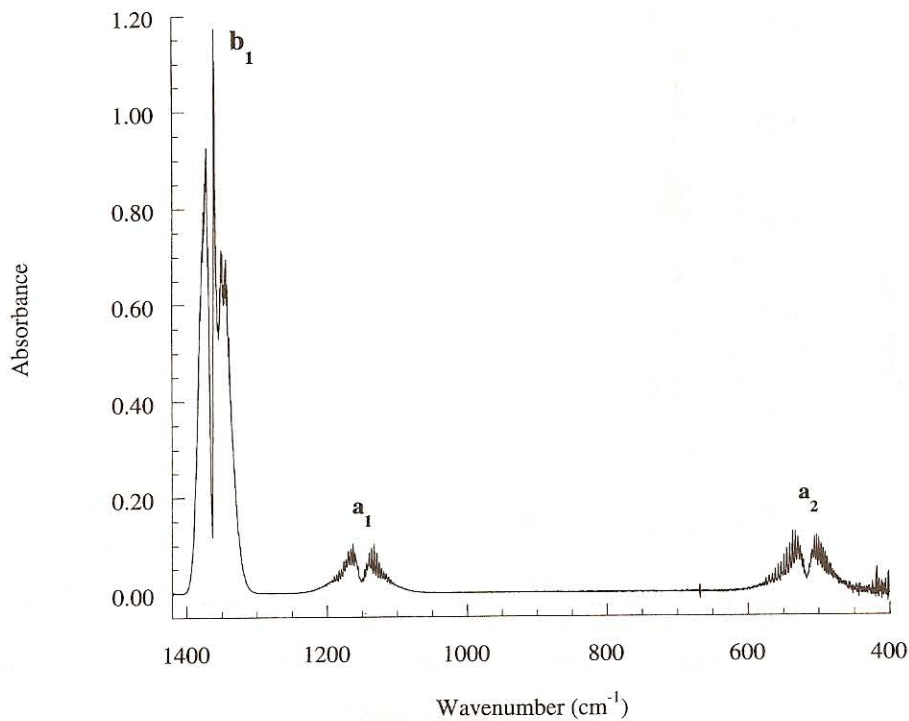


Fig. 8. FT-IR spectrum of sulfur dioxide (SO_2) in air under quasi-static conditions at 1.0cm^{-1} resolution with a gas pressure of 200 Torr when the gas passes through Copper tubing.

Table 8

FT-IR spectral peaks of sulfur dioxide (SO_2) in air under flow-through conditions at a gas pressure of 80 Torr using a 10-m path length multipass gas cell

Mode	ν (cm^{-1})	Absorbance ^a			
		Aluminum	Copper	Stainless-steel	Teflon
$b_1(\text{SO}_2)$	1373.71	0.209	0.927	0.222	0.105
	1359.60	0.214	1.194	0.227	0.108
	1349.90	0.163	0.715	0.173	0.083
$a_1(\text{SO}_2)$	1164.80	0.019	0.103	0.021	0.011
	1135.90	0.016	0.102	0.018	0.009
$a_2(\text{SO}_2)$	532.26	0.022	0.128	0.024	0.014
	503.34	0.024	0.119	0.025	0.016

^a The uncertainty in the measurement of absorbance is 0.001.

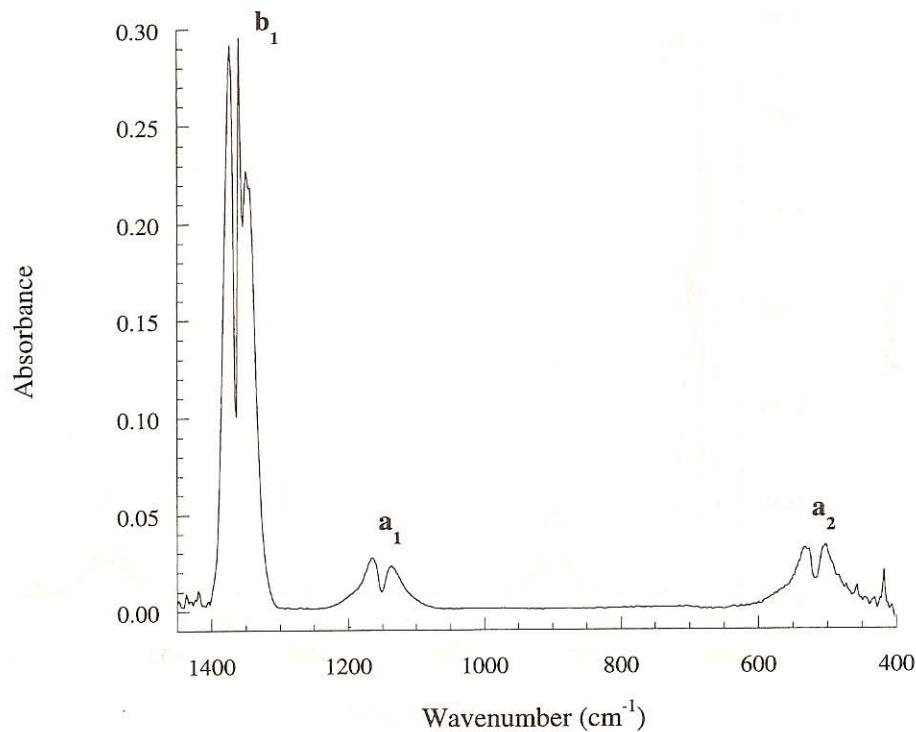


Fig. 9. FT-IR spectrum of sulfur dioxide (SO₂) under flow-through conditions at 4.0cm⁻¹ resolution with a gas pressure of 80 Torr when the gas passes through copper tubing.

4. Conclusion

Nitrogen dioxide, sulfur dioxide and hydrogen chloride are trace gases that are present in the atmosphere and are important for the understanding of stratospheric ozone depletion, global warming and photochemical smog formation [2]. FT-IR spectroscopy has aided in the identification of such multiple pollutants in the atmosphere. Owing to the reactivity of various sample tubings that are used as device materials for QCM/SAW investigations, different tubings were used to check the acidity/basic nature of the sample gases in relation to various atmospheric trace gases. For example, both nitrogen dioxide (NO₂) and nitric acid (HNO₃) showed strong reactivity toward materials like aluminum and copper, whereas sulfur dioxide (SO₂) showed very little variation in absorbance when different tubings, such as aluminum, copper, stainless-steel and Teflon were used. Based on our results we would recommend the use of Teflon for QCM/SAW measurements of trace atmospheric species.

FT-IR spectroscopy has provided accurate values for the rotational constants for both ¹H³⁵Cl and ¹H³⁷Cl molecules, which agree with the values reported in the literature, and also allowed an accurate determination of the temperature of the gas in the 10-m path length cell used for recording the absorption spectra of trace amounts of molecular species.

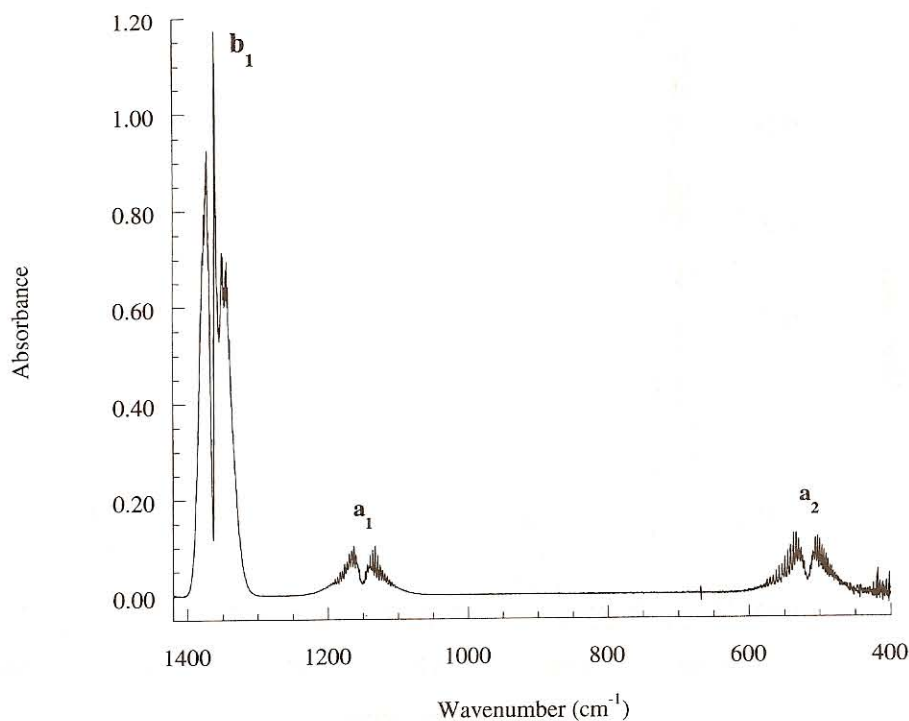


Fig. 8. FT-IR spectrum of sulfur dioxide (SO_2) in air under quasi-static conditions at 1.0cm^{-1} resolution with a gas pressure of 200 Torr when the gas passes through Copper tubing.

Table 8

FT-IR spectral peaks of sulfur dioxide (SO_2) in air under flow-through conditions at a gas pressure of 80 Torr using a 10-m path length multipass gas cell

Mode	ν (cm^{-1})	Absorbance ^a			
		Aluminum	Copper	Stainless-steel	Teflon
$b_1(\text{SO}_2)$	1373.71	0.209	0.927	0.222	0.105
	1359.60	0.214	1.194	0.227	0.108
	1349.90	0.163	0.715	0.173	0.083
$a_1(\text{SO}_2)$	1164.80	0.019	0.103	0.021	0.011
	1135.90	0.016	0.102	0.018	0.009
$a_2(\text{SO}_2)$	532.26	0.022	0.128	0.024	0.014
	503.34	0.024	0.119	0.025	0.016

^a The uncertainty in the measurement of absorbance is 0.001.

Acknowledgements

Financial support from the Center for the Study of Terrestrial and Extraterrestrial Atmospheres (# NASA NAGW-2950), the NASA Lewis Research Center (# NAG3-1677) and the US Environmental Protection Agency's Office of Exploratory Research (# R819720-01) is gratefully acknowledged.

References

- [1] Rafiu AA, Okabe H, Misra P. FTIR spectroscopy of HNO_3 and NO_2 relevant to stratospheric wake analysis. In: First NASA Student Conference, North Carolina A&T State University, 1996.
- [2] Sigrist MW. Introduction to environmental sensing. In: Sigrist MW, editor. Air monitoring by spectroscopic techniques. John Wiley & Sons, 1994. p. 1–26.
- [3] Coleman PB. Practical sampling techniques for infrared analysis. Boca Raton, FL: CRC Press, 1993.
- [4] Herzberg G. Electronic spectra and electronic structure of polyatomic molecules. Malabar, FL: Krieger Publishing Company, 1989.
- [5] Cross PC, Hainer RM, King GW. *J Chem Phys* 1944;12:210.
- [6] Cabana A, Laurin M, Pepin C, Lafferty WJ. *J Mol Spectrosc* 1976;59:13.
- [7] Dana V. *Rev Phys Appl* 1974;9:71.
- [8] Dana V, Fontanella JC. *Nouv Rev Opt* 1973;4:237.
- [9] Hurlock SC, Lafferty WJ, Narahari Rao K. *J Mol Spectrosc* 1974;50:246.
- [10] Hurlock SC, Narahari Rao K, Weller LA, Yin PKL. *J Mol Spectrosc* 1974;48:372.
- [11] Cabana A, Laurin M, Lafferty WJ, Sams RL. *Can J Phys* 1975;53:1902.
- [12] Semmoud-Monnanteuil N, Colmont J-M, Perrin A, Flaud J-M, Camy-Peyret C. *J Mol Spectrosc* 1989;134:176.
- [13] Perrin A, Flaud J-M, Camy-Peyret C, Vasserot A-M, Guelachvili G, Goldman A, Murcay FJ, Blatherwick RD. *J Mol Spectrosc* 1992;154:391.
- [14] Olman MD, Hause CD. *J Mol Spectrosc* 1968;26:241.
- [15] Blank RE, Hause CD. *J Mol Spectrosc* 1970;34:478.
- [16] Blank RE, Olman MD, Hause CD. *J Mol Spectrosc* 1970;33:109.
- [17] Lafferty WJ, Sams RL. *Mol Phys* 1974;28:861.
- [18] Sams RL, Lafferty WL. *J Mol Spectrosc* 1975;56:399.
- [19] Perrin A, Flaud J-M, Camy-Peyret C, Murray FJ, Blatherwick RD, Rinsland CP. *J Mol Spectrosc* 1993;160:456.
- [20] Guelachvili G, Niay P, Bernage P. *J Mol Spectrosc* 1981;85:271.
- [21] Pine AS, Fried A. *J Mol Spectrosc* 1985;114:148.
- [22] Rotham LS, Gamache RR, Tipping RH, Rinsland CP, Smith MAH, Benner DC, Malathy Devi V, Flaud J-M, Camy-Peyret C, Perrin A, Goldman A, Massie ST, Brown LR, Toth RA. *J Quant Spectrosc Radiat Transfer* 1992;48:469.
- [23] Rinsland CP, Smith MAH, Goldman A, Malathy Devi V, Benner DC. *J Mol Spectrosc* 1993;159:274.
- [24] Hollas JM. *Modern Spectroscopy*. New York: John Wiley & Sons, 1986.
- [25] Bernath PF. *Spectra of atoms and molecules*. New York, NY: Oxford University, 1995.
- [26] Herzberg G. *Electronic spectra and electronic structure of diatomic molecules*. Malabar, FL: Krieger Publishing Company, 1989.
- [27] Morino Y, Kikuchi Y, Saito S, Hirato E. *J Mol Spectrosc* 1964;13:95.
- [28] Van Riet R. *Ann Soc Sci Brussels* 1964;78:237.
- [29] Gebbie HA, Stone NWB, Topping G, Gora EK, Clough SA, Kneizys FX. *J Mol Spectrosc* 1966;19:7.
- [30] Steenbeckeliers G. *Ann Soc Sci Bruxelles* 1968;82:331.
- [31] Saito S. *J Mol Spectrosc* 1969;30:1.
- [32] Guelachvili G, Ulenikov ON, Ushavkova GA. *J Mol Spectrosc* 1984;108:1.

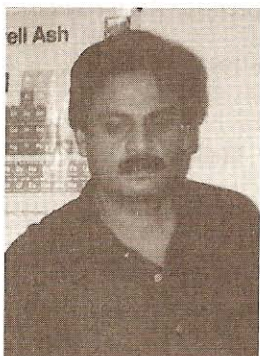
- [33] Sattler JP, Worchesky IL, Lafferty WJ. *J Mol Spectrosc* 1981;88:364.
[34] Flaud J-M, Perrin A, Salah LM, Lafferty WJ, Guelachvili G. *J Mol Spectrosc* 1993;160:272.
[35] Barbe A, Jouve P. *J Mol Spectrosc* 1971;38:273.
[36] Vanek MD, Wells JS, Maki AG, Burkholder JM. *J Mol Spectrosc* 1990;141:346.



Dr. C. Haridass is a Postdoctoral Research Associate in the Laser Spectroscopy Laboratory, Department of Physics and Astronomy, Howard University, Washington, DC 20059. His research interest is in the area of electronic spectroscopy of molecules and Fourier Transform spectroscopy of atmospherically significant molecules.



Mr. Abdullahi Aw-Musse is a graduate student working for his Ph.D. degree in the Department of Physics and Astronomy, Howard University, Washington, DC 20059. His research interest is in the area of Fourier Transform spectroscopy of atmospherically significant molecules.



Dr. P. Misra is a Professor in the Department of Physics and Astronomy, Howard University, Washington, DC 20059. He is also an Associate Principal Investigator in the Center for the Study of Terrestrial and Extraterrestrial Atmospheres (CSTEAs). His research interest is in the area of laser spectroscopy of free radicals of relevance to the elucidation of atmospheric and combustion phenomena.



Mr. John Jordan is an undergraduate student working for his B.S.E.E. degree in the Department of Electrical Engineering, Howard University, Washington, DC 20059. His research interest is in the area of spectroscopy of stable and transient molecular species of significance for the understanding of terrestrial and extraterrestrial atmospheres.