Detection of Ammonia and Deuterated Hydrocarbons in Exhaust Gas by Infrared Absorption Spectroscopy during Wall Conditioning[*]

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To detect ammonia and deuterated hydrocarbons in exhaust gas from the Large Helical Device (LHD), infrared absorption spectrometry, FTIR with a long optical path gas cell, was applied. Ammonia (NH_3) and deuterated hydrocarbons ($C_xH_yD_z$) could be detected during the first operations of wall baking at 368 K and the D_2 glow discharge conducted after vacuum vessel closure. The concentration of ammonia increased with increasing baking temperature, and deuterated ammonia was not detected. Thus, the ammonia, which likely originated from sweat of workers produced during vacuum vessel maintenance activities, was released from the vacuum vessel wall. Hydrocarbons were likely produced by chemical sputtering of carbon tiles and were deuterated by a hydrogen isotope exchange reaction due to D_2 glow discharge, while H_2O was released from the vacuum vessel during wall baking. It was confirmed that ammonia and various types of deuterated hydrocarbons could be measured discriminately by an FTIR spectroscopy system using a long optical path gas cell.

1. Introduction

The Large Helical Device (LHD), which has a large superconducting magnet system, has been conducting high-temperature plasma experiments using hydrogen (H) and deuterium (D) since March 2017 [1,2]. An ion temperature of 10 keV was achieved in the first deuterium plasma experimental campaign of the LHD. In a high-temperature plasma experiment, removal of the divertor heat load is one of the critical issues to realize a fusion reactor. To protect divertor tiles from damage due to local heat loads, the seeding of gaseous impurities, such as neon, argon, krypton, xenon, and nitrogen, is mandatory. As one of the seeding gases, nitrogen not only reduces the local heat loads but may also improve plasma confinement [3]. However, the formation of compounds from nitrogen and hydrogen isotopes is possible. As one of these compounds, ammonia (NQ_3, Q = H, D, T) formation could be a serious issue for cryosorption pumps and the exhaust detritiation system (EDS), which removes tritium from the exhaust gas.

Plasma experiments regarding the seeding of nitrogen in the divertor region have been conducted by ASDEX-Upgrade (AUG) and Joint European Torus (JET) [3–7]. In these studies, ammonia formation was observed in the vacuum vessel. Ammonia can be detected by various gas an-

alytical techniques. Typical analytical techniques include gas chromatography (GC) and use of a residual gas analyzer (RGA) with a quadrupole mass spectrometer [8–12]. A GC system would not be the preferred analytical technique to detect ammonia owing to its high polarity and corrosive attributes, although ammonia has been detected by this method [10]. Also, a normal GC system cannot discriminate between hydrogen isotope compounds, such as deuterated compounds. An RGA system is a candidate to analyze gaseous compositions containing hydrogen isotope species and compounds. An RGA system has been applied to observe ammonia in AUG and JET [12]. When considering detection of hydrocarbons (C_xQ_y), water vapor (Q_2O), and ammonia (NQ_3) gas composition, it is important to note that the mass number of these gases is the same as that of some hydrogen isotope compounds, as summarized in Table 1. Fragments of these gas species overlap

Table 1 Mass number of typical hydrocarbons (C_xQ_y), water vapor (Q_2O), and ammonia (NQ_3). "Q" is expressed as hydrogen isotopes H and D.

Mass number	16	17	18	19	20	28	32
Chemical forms	CH_4	CH_3D	H_2O	HDO	D_2O	N_2	O_2
		NH_3	CH_2D_2	CHD_3	CD_4	CO	C_2D_4
			NH_2D	NHD_2	ND_3	C_2H_4	
						C_2D_2	

Table 2 Typical absorption wavenumbers of H and D in various hydrocarbons and ammonia [20, 21].

Chemical forms (Q = H, D)	Wave number (cm⁻¹)			Mode	
	H	HD	D	H, D	HD
methane (CQ₄)	3018.9	1155/1090/1036 (CH_3D/CH_2D_2/CHD_3)	2259	degenerate stretching vibration	CQ rocking vibration
ethane (C₂Q₆)	2954	2098/2912 (CH_3CD_3)	2083	symmetrical stretching vibration	
ethylene (C₂Q₄)	949.3		720	CQ₂ wagging vibration	
acetylene (C₂Q₂)	730.3	678 (CHCD)	536.9	CQ bending vibration	
ammonia (NQ₃)	968		748	symmetrical deformation vibration	

each other. Therefore, it would be difficult to discriminate between these chemical compositions using an RGA system.

In this study, we proposed the application of infrared absorption spectrometry to analyze complex gas compositions in exhaust gas containing ammonia and deuterated hydrocarbons. Additionally, the exhaust behaviors of ammonia and deuterated hydrocarbons during wall baking operations and D_2 glow discharge are discussed.

2. Experimental Setup

2.1 Monitoring exhaust gas from the LHD and the wall conditioning procedure

After a deuterium plasma experiment in the LHD is started, tritium is exhausted from the vacuum vessel. An EDS was installed prior to performing the deuterium plasma experiment [13]. Because the EDS is connected to all exhaust gas lines from the LHD system, the inlet of the EDS is suitable for observing exhaust gas composition, including hydrogen isotopes. To observe tritium and gas composition in the exhaust gas, various gas analysis instruments belonging to a GC system, including an RGA system, a dew point hygrometer, an optical-type hydrogen sensor, an ionization chamber, an original water bubbler system, and a Fourier transform infrared (FTIR) spectroscopy system with a long optical path gas cell, were installed and have been previously operated [14, 15]. Using these instruments, the exhaust behavior of tritium from the LHD was revealed in the first deuterium plasma experimental campaign [16, 17]. Studies have shown that the exhaust gas composition during plasma experiments varies depending on the operating conditions. However, the dew point in the exhaust gas is normally below −30°C.

As for the wall conditioning operation in the LHD, a wall baking operation at 368 K with D_2 glow discharge was performed. The glow discharge was operated in constant current mode, and the discharge current was set to 10 A. The gas pressure in the D_2 glow discharge was adjusted to ∼ 1.0 - 1.2 Pa. Two electrodes (G1 and G2), which were installed at the opposite port in the torus vacuum vessel,

were used during glow discharge operation.

2.2 FTIR spectroscopy system [18]

In a previous study, extremely low concentrations of hydrocarbons, on the order of sub-ppm, were successfully detected using an FTIR spectroscopy system (Perkin Elmer, Frontier FTIR) with a long optical path gas cell (PIKE Technologies, PN: 163-1674). Details of the analytical system and the measurement conditions of the FTIR spectroscopy system combined with a long optical path gas cell are described in a previous article [18]. In this study, the measured wavenumber range was 650 to 3500 cm⁻¹, the scan number was set to 50, the wavenumber resolution was set to 1 cm⁻¹, and the optical path length in the gas cell was fixed to 16 m. The Atmospheric Vapor Compensation algorithm, which is an advanced digital filtering algorithm designed to compensate for H_2O absorption [19], was used while obtaining measurements.

The following operational sequence was employed in this study: (1) the gas cell was evacuated to less than −95 kPa (G) (for 5 min), (2) the gas cell was filled with sample gas to atmospheric pressure (for 5 min), and (3) measurements were acquired using the FTIR system (for 15 min). The total measurement interval was 25 min. The background spectrum was measured before starting the wall conditioning operation. Typical absorption wavenumbers of H and D in various hydrocarbons and ammonia [20, 21] are summarized in Table 2.

3. Results and Discussion

3.1 FTIR spectra of ammonia and deuterated hydrocarbons during wall baking and D_2 glow discharge

The analysis of exhaust gas composition was conducted during wall baking at 368 K and with D_2 glow discharge. Because of the first wall baking operation after vacuum vessel closure, the water vapor concentration at the inlet of the EDS was relatively high, approximately 1600 ppm (dew point: −17°C). Figure 1 shows the FTIR absorption spectrum obtained during wall baking at 368 K
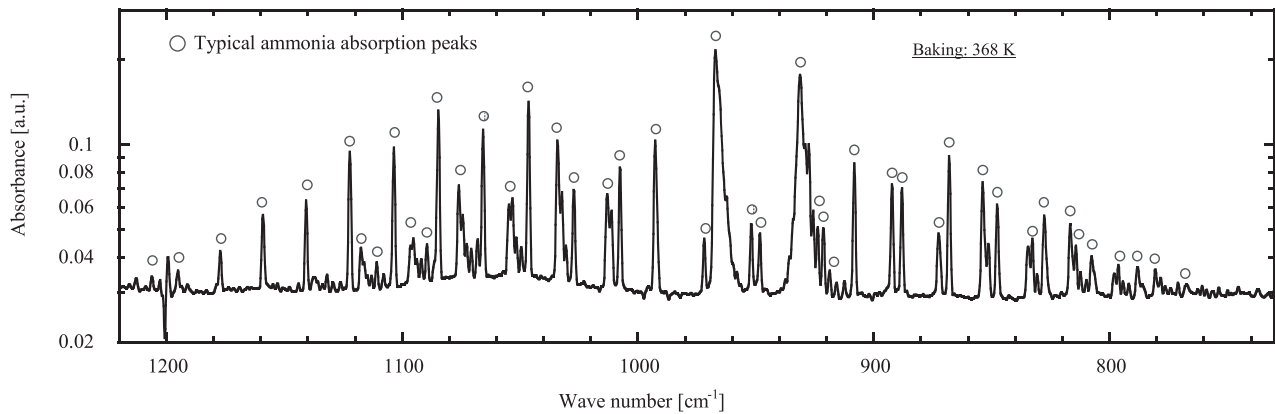
Fig. 1   FTIR absorption spectrum obtained during the wall baking operation. Circles indicate typical ammonia absorption peaks.
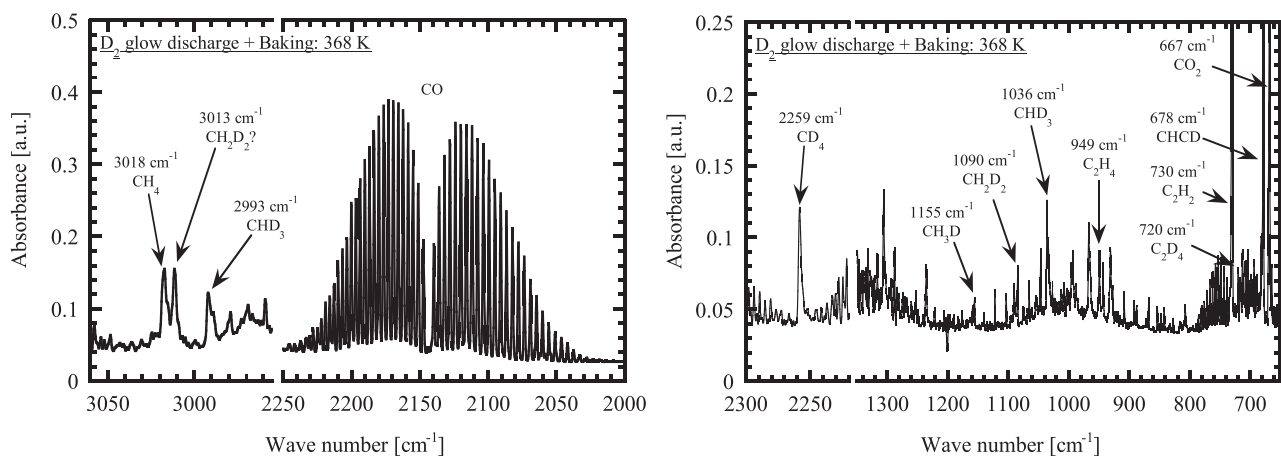

Fig. 2   Example FTIR exhaust gas spectra during wall baking at 368 K and D_2 glow discharge operation in the LHD. Left: measurements at 2000 - 2250 cm^{-1} (CO) and 2955 - 3060 cm^{-1} (CH_yD_{4-y}); right: measurements at 650 - 1350 cm^{-1} ($C_xH_yD_z$ and CO_2) and 2220 - 2300 cm^{-1} (CD_4).

at a wavenumber range of 720 - 1220 cm^{-1}. Several absorption peaks are observed in this range, and the measured spectrum is consistent with absorption peak data of ammonia. It was found that exhaust gas created during the first baking operation, after vacuum vessel closure, contained ammonia. On the other hand, the absorption spectrum of deuterated ammonia (ND_3) was not observed for this operating condition.

Figure 2 shows FTIR absorption spectrum during D_2 glow discharge and wall baking at 368 K. CO, CO_2, and deuterated hydrocarbons are observed. CO and CO_2 are known to be produced and observed during the glow discharge operation [18, 22]. Hydrocarbons are produced by chemical sputtering of carbon tiles during the hydrogen isotope glow discharge operation. In a previous study [18], however, deuterated hydrocarbons ($C_xH_yD_z$) were not detected during D_2 glow discharge between LHD plasma experiments. Thus, the vacuum vessel is cleaned by the plasma experiments and wall conditioning operations, lowering impurity components such as water vapor. On the other hand, in this study, water vapor (H_2O) is released

from the vacuum vessel wall during the wall baking operation. Thus, deuterated hydrocarbons are produced by a hydrogen isotope exchange reaction between hydrocarbons (C_xD_y) and water vapor (H_2O).

3.2   Release behavior of ammonia during baking

Figure 3 shows the variation of wall temperature and absorbance of ammonia, at 968 cm^{-1}, during the baking process. The absorption intensity is defined as the height subtracted at the lowest point at one side of the peak signal from the peak signal level. The D_2 glow discharge operation was conducted from time 9:30 to 16:30, as indicated in Fig. 3. The wall baking temperature was constant at time 8:00. The ammonia signal increased with increasing wall baking temperature. This behavior suggests that ammonia was released from the vacuum vessel wall. Since deuterated ammonia was not detected, the source of ammonia is the sweat of workers left in the chamber during maintenance activities over a 4-month period. After beginning the
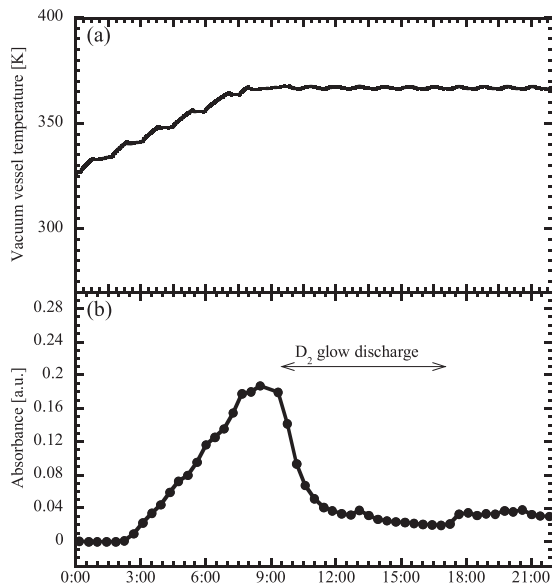
Fig. 3 Variations of (a) LHD vacuum vessel temperature and (b) absorbance of NH_3 at 968 cm^1.

glow discharge operation, the ammonia signal decreased rapidly. Ammonia is likely decomposed by the plasma of the glow discharge. On the other hand, the ammonia in the exhaust gas was not detected during the N_2 seeding operation in the LHD plasma experiment. This operation would not produce a sufficient amount of ammonia to be detected by the FTIR system during the plasma experimental conditions of the diverter region in the LHD.

3.3 Production of deuterated hydrocarbons during D_2 glow discharge during wall baking

Figure 4 shows variations of current and voltage during the glow discharge operation and the corresponding absorbance signal of deuterated hydrocarbons. The monitored absorption signals are typical wavenumbers of each hydrocarbon, as shown in Table 2. The wall baking operation at 368 K continued during the glow discharge operation. In the LHD, two electrodes, which were installed at the opposite port in the LHD torus vacuum vessel, were used for glow discharge operation, as described in Section 2.1. The G1 and G2 in the caption of Fig. 4 indicate the electrode number.

The first half of the glow discharge was unstable and the voltage fluctuated considerably from 100 to 400 V, as shown in Fig. 4. Thus, the current was readjusted to 5 A in the latter half of the operation to create stable discharge. Various types of deuterated hydrocarbon, CH_xD_{4-x}, C_2H_4, C_2D_4, C_2H_2, and CHCD, were detected in the first half of the D_2 glow discharge process. The absorption wavenumber of C_2D_2 (536.9 cm^{-1}) was outside of the measurement range. As mentioned in Section 3.1, deuterated hydrocarbons would be generated by the hydrogen isotope exchange reaction between water vapor (H_2O) released by
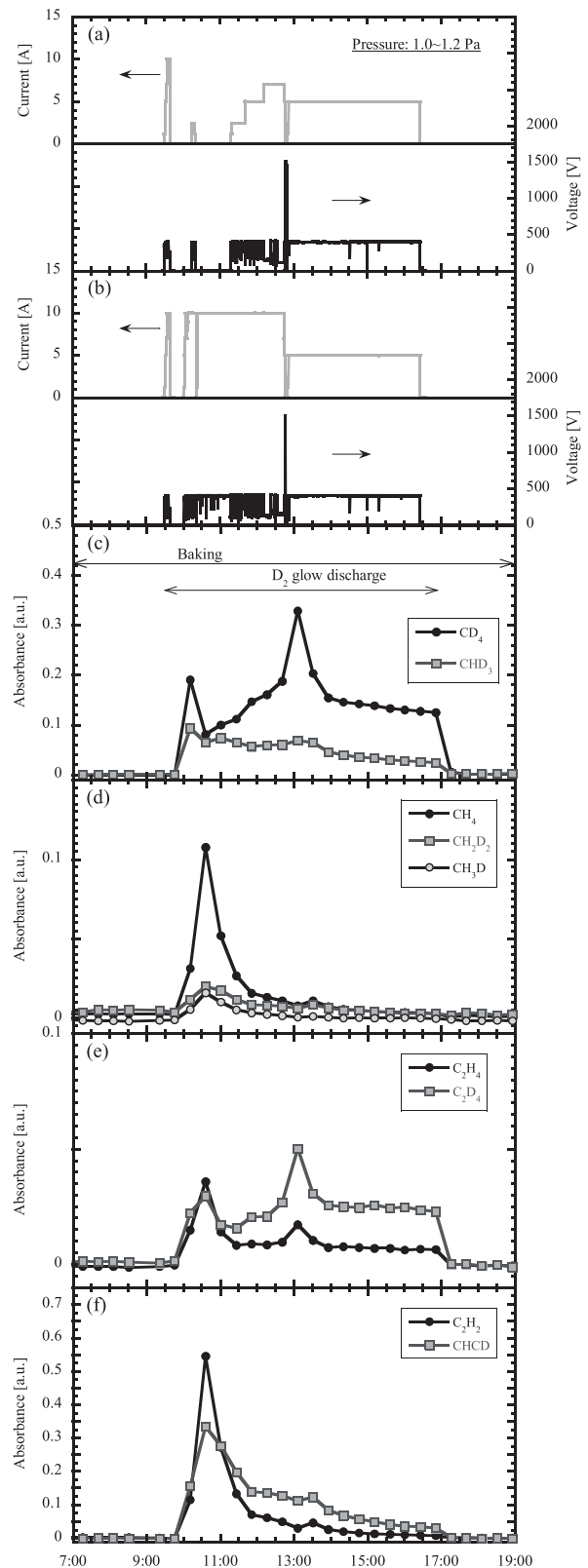

Fig. 4 Variations of (a) the current and voltage of glow discharge operation by G1 electrode, (b) by G2 electrode, (c) absorbance of CD_4 and CHD_3, (d) absorbance of CH_2D_2, CH_3D and CH_4, (e) absorbance of C_2H_4 and C_2D_4, (f) absorbance signal of C_2H_2 and CHCD.

wall baking and C_xD_y produced by chemical sputtering. In the unstable operation region, acetylene, which was not detected during the glow discharge operation in a previous study [18], was observed. Additionally, the ratio of hydrogen atoms in the produced hydrocarbons, C_xQ_y, was higher. When the voltage was unstable, the glow discharge would occur locally and the condition of chemical sputtering likely changed. In the latter half of glow discharge, the voltage was stable, and methane and ethylene were steadily produced. The ratio of deuterium atoms in the produced hydrocarbons also tended to be higher, although the absorption coefficients of deuterated hydrocarbons were different. The chemical forms and production rate of hydrocarbons may be dependent on current and voltage in the glow discharge.

4. Summary

To investigate the behavior of ammonia and deuterated hydrocarbons in exhaust gas from the LHD, the gas composition was analyzed by FTIR spectroscopy with a gas cell. Ammonia and deuterated hydrocarbons were detected during the first wall baking operation at 368 K and during the D_2 glow discharge operation after the vacuum vessel closure. Since deuterated ammonia was not detected during the wall baking operation, the ammonia was released from the vacuum vessel wall and its source is likely the sweat of workers produced during vacuum vessel inspection and maintenance work. Hydrocarbons were produced by the chemical sputtering of carbon tiles and was deuterated by the hydrogen isotope exchange reaction between hydrocarbons (C_xD_y) and H_2O released during wall baking. It was confirmed that various types of deuterated hydrocarbons could be detected discriminately using the FTIR system with a long optical path gas cell. For future work, the calibration gas of deuterated hydrocarbons and ammonia is needed for quantitative measurement.

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