Preliminary study on direct measurements and diagnostics for chemical reaction dynamics of NO$_x$ by using laser wavelength modulation spectroscopy

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Studies on the kinetics of gas-phase chemical reactions currently rely on calculations or simulations and lack simple, fast, and accurate direct measurement methods. We developed a tunable laser molecular absorption spectroscopy measurement system to achieve direct measurements of such reactions by using wavelength modulated spectroscopy and performed online measurements and diagnostics of molecular concentration, reaction temperature, and pressure change during the redox reaction of ozone with nitrogen oxides (NO$_x$) with 0.1 s temporal resolution. This study provides a promising diagnostic tool for studying gas-phase chemical reaction kinetics.
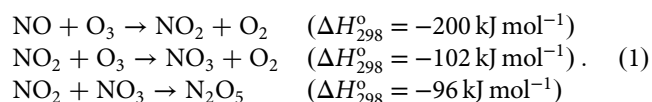
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1. Introduction

Nitrogen oxides (NO$_x$) emitted during the combustion of fossil fuels are the main cause of photochemical smog and acid rain[1]. To reduce the impact of NO$_x$ on the environment and human health, the oxidation of NO$_x$ to the highly soluble N$_2$O$_5$ by ozone (O$_3$) injection and then removal by wet process is an effective DeNO$_x$ technology[2]. Therefore, detailed measurements of molecular concentration, reaction temperature, and pressure changes during the reaction of NO$_x$ oxidation by O$_3$ injection can help to understand more deeply the chemical kinetics of this reaction process, provide data reference for the reaction process, and supply support to the cognition of the reaction mechanism and the optimization of the reaction conditions.

During the oxidation of NO$_x$ by injection of O$_3$, the chemical reaction occurs as[3]

$$
\begin{aligned}
\mathrm{NO} + \mathrm{O_3} &\rightarrow \mathrm{NO_2} + \mathrm{O_2} & (\Delta H^{\mathrm{o}}_{298} = -200\,\mathrm{kJ\,mol^{-1}}) \\
\mathrm{NO_2} + \mathrm{O_3} &\rightarrow \mathrm{NO_3} + \mathrm{O_2} & (\Delta H^{\mathrm{o}}_{298} = -102\,\mathrm{kJ\,mol^{-1}})\,. \\
\mathrm{NO_2} + \mathrm{NO_3} &\rightarrow \mathrm{N_2O_5} & (\Delta H^{\mathrm{o}}_{298} = -96\,\mathrm{kJ\,mol^{-1}})
\end{aligned} \quad (1)
$$

O$_2$, NO, and NO$_2$ are the key substances for this reaction, and the accurate determination of these substances during the reaction is necessary to understand the reaction process of NO$_x$ oxidation by O$_3$. For the diagnosis of these substances, conventional

extraction sampling probes combined with gas chromatography or mass spectrometry are usually used[4], however, the relatively long response time, invasiveness, and potential secondary chemical reactions during the sampling process limit their application for chemical reaction process measurements. Optical sensing addresses these issues by providing non-invasive measurements[5]. In particular, laser absorption spectroscopy (LAS) is one of the key optical diagnostic techniques for *in situ*, rapid, quantitative, and species-specific measurements[6]. The measurement of NO$_x$-related chemical reaction processes based on LAS technology has been reported. For example, Almodovar *et al.*[7] used tunable diode LAS (TDLAS) for *in situ* detection of high-temperature gas temperature and NO concentration measurements, further explaining the temperature dependence of NO collisional spreading. Zeng *et al.*[8] quantified the concentrations of key intermediates CO, N$_2$O, and NO and gas temperatures during the combustion of ammonium dinitramide (ADN) using TDLAS in the near and mid-infrared bands. Shang *et al.*[9] determined the key product NO of CH$_3$NO$_2$ by the TDLAS technique and investigated the pyrolysis process of CH$_3$NO$_2$ in heated excitation tubes at about 3.5 atm and 1013–1418 K. However, studies on the measurement of key substances during NO oxidation by O$_3$ are very limited.

In this work, we reported a spectral measurement system for the O$_3$ oxidizing NO reaction process. Using near and

mid-infrared tunable LAS, the O_3 oxidizing NO reaction process was continuously detected, the changes in temperature, pressure as well as the concentrations of O_2, NO, and NO_2 in the reaction gas cell were recorded, and the experimental data were analyzed and explained in the context of the reaction mechanism. The feasibility of this spectral measurement system was verified by the spectral measurement experiment of the O_3 oxidizing NO reaction process.

2. Experiments and Methods

The schematic diagram of our designed experimental system for spectroscopic measurement of the NO_x oxidation reaction process by O_3 is shown in Fig. 1. The system consists of NO and NO_2 spectral measurement units, O_2 spectral measurement units, and O_3 electrochemical measurement units. The reaction is carried out in a homemade reaction gas cell with a volume of $199\,\text{mm} \times 100\,\text{mm} \times 104\,\text{mm}$. To facilitate the passage of the measurement beam and reduce the light intensity attenuation, CaF_2 window mirrors are installed on the wall of the gas cell. The detailed configuration parameters of the experimental system are shown in Table 1. It is noteworthy that, to realize the simultaneous measurement of NO and NO_2, the measurement method of time-scanning and wavelength modulation in combination was used for Laser II and Laser III, and the modulated waveforms are shown in Fig. 1(a). The resulting NO and NO_2 absorption spectra are separated from each other and do not interfere with each other, so the time-sharing sawtooth scanning method does not produce mixed spectra and reduces the average luminescence time of the quantum cascade laser (QCL) and heat generation, which improves the thermal stability of the system. Compared with frequency division multiplexing techniques that modulate each laser at different frequencies, the time-division scanning combined with wavelength modulation is less complex, eliminating more background noise due to the sum of

Table 1. Experimental System Configuration Parameters.

Gas	Laser	Measurement Method	Wavenumber (cm^{-1})	Detection Sensitivity (mol/L)
O_2	DBR, Photodigm	WMS-2f/1f	13142.6	6.13×10^{-6}
NO_2	QCL, Hamamatsu	WMS-2f/1f	1629.85	4.91×10^{-6}
			1630.33	
NO	QCL, Hamamatsu	WMS-2f/1f	1900.07	1.06×10^{-5}
O_3		Electrochemical	–	4.09×10^{-6}

the received light from multiple lasers and demodulating the signal to noise ratio higher and simpler.

The detector located on the other side of the gas cell transmits the received optical signals to a homemade digital lock-in amplifier (DLIA), which is demodulated by the DLIA to obtain the WMS-2f/1f signals of the O_2, NO_2, and NO absorption spectra, as shown in Figs. 1(c) and 1(d). The spectral measurement part monitors the temperature, pressure, NO, NO_2, and O_2 concentrations in the gas cell during the reaction process. An electrochemical O_3 sensor (BOSEAN, BH-90) is placed at the gas outlet of the reaction gas cell to monitor the O_3 concentration.

Two reaction gases are prepared before the experiment. The NO used is prepared by diluting NO gas of 99.5% purity in a gas cylinder with nitrogen gas; meanwhile, the NO concentration is monitored by the NO spectral measurement part of the system. The O_3 to be injected is generated by a dielectric discharge type O_3 generator in a gas cell with a volume of $342\,\text{mm} \times 300\,\text{mm} \times 300\,\text{mm}$ and the concentration is monitored by an O_3 sensor (BOSEAN, BH-90). After the experiment starts, O_3 is injected into the reaction gas cell by a micro-pump (QIHAI, VBY21606).
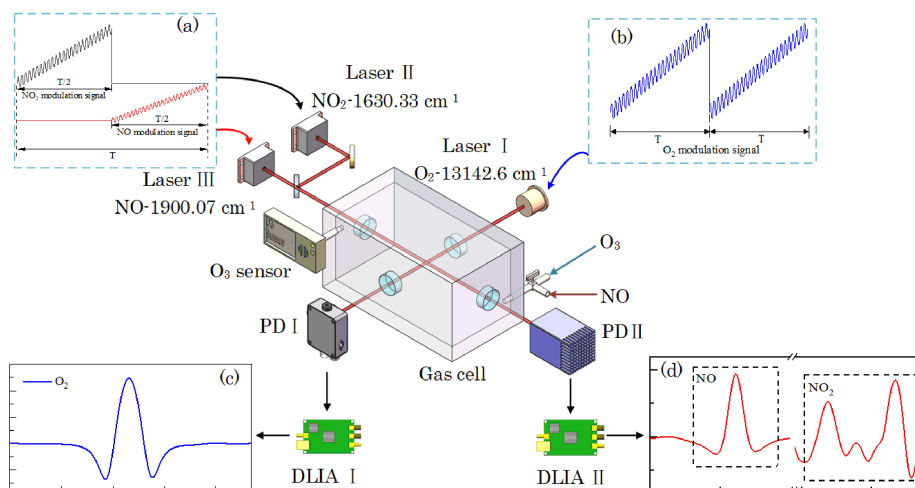

Fig. 1. Schematic diagram of the experimental system: (a) NO_x measurement modulation waveform; (b) O_2 measurement modulation waveform; (c) WMS-2f/1f signal of demodulated O_2 absorption spectra; (d) WMS-2f/1f signal of demodulated NO and NO_2 absorption spectra.

The spectral measurement data processing algorithm is based on Levenberg-Marquardt (L-M) nonlinear least-squares fitting[10], and the measured signal is iterated with the simulated signal by setting the initial parameters of NO_2 spectral lines until the algorithm converges to obtain the best-fit parameters, and the temperature, pressure, and NO_2 concentration in the gas cell are obtained from the molecular absorption spectroscopy bilinear temperature measurement[11] and gas parameter inversion theory[12]. When the temperature and pressure of the gas are obtained, the wavelength modulation spectroscopy (WMS)-2f/1f profiles of NO and O_2 measured in the same cycle are linearly fitted to the standard WMS-2f/1f signals at the
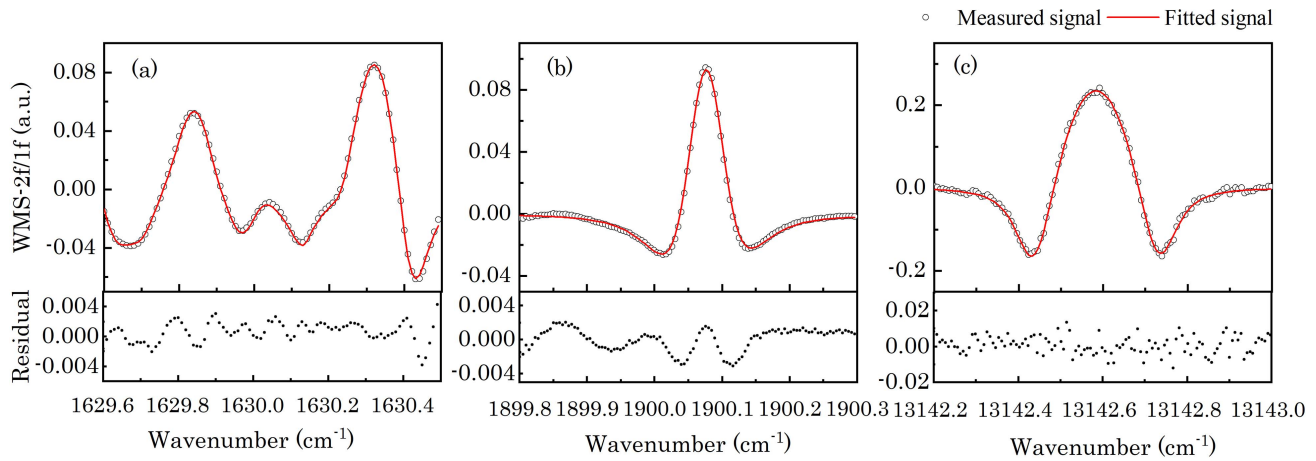

Fig. 2. Fitting results and residuals of WMS-2f/1f for NO_2, NO, and O_2 absorption spectra: (a) 0.14% relative root mean square (RMS) for the NO_2 spectra; (b) 0.17% relative RMS for the NO spectra; (c) 0.21% relative RMS for the O_2 spectra.
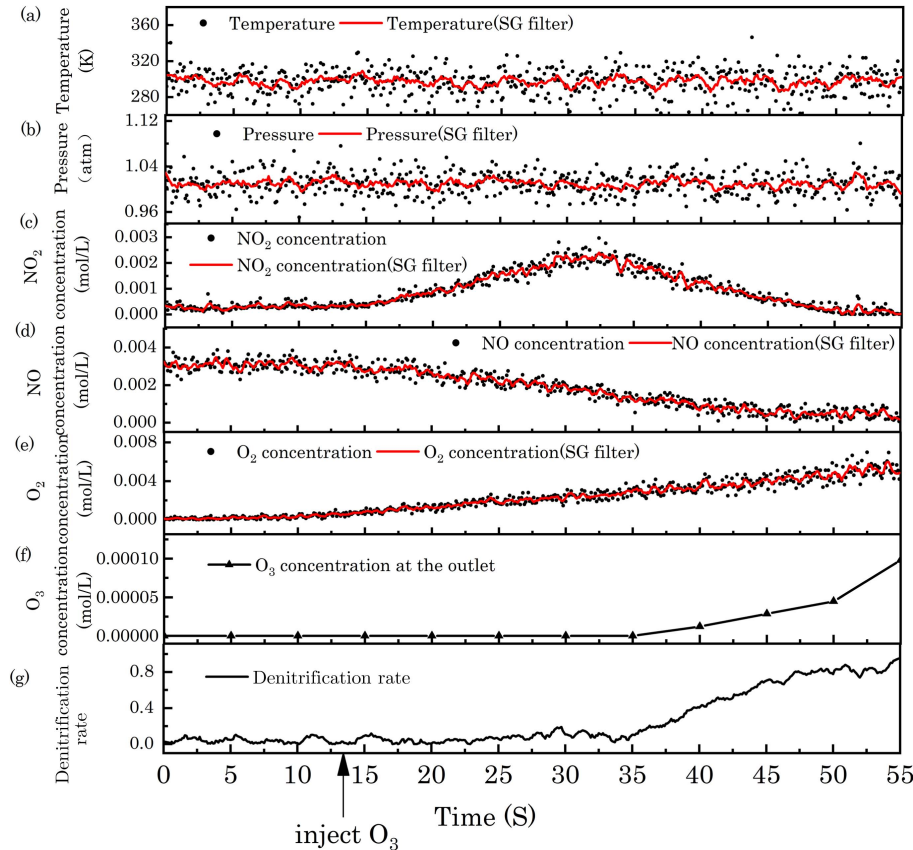

Fig. 3. Measurement results of O_3 oxidizing NO reaction process: (a) temperature; (b) pressure; (c) NO_2 concentration; (d) NO concentration; (e) O_2 concentration; (f) O_3 concentration; (g) denitrification rate.

corresponding temperature and pressure to obtain the concentrations of NO and O_2 in the reaction gas cell[13].

3. Results and Discussion

The measured raw signals obtained from the spectral measurement unit and their fitting results are shown in Fig. 2. The inverse performance of the gas parameters based on the fitting results is shown in Fig. 3, and the results were smoothed using a Savitzky–Golay filter (filter parameters: eight window points, order two). O_3 started to be injected at about 12 s; after that the NO concentration in the gas cell started to decrease, while the concentrations of NO_2 and O_2 increased; after the NO_2 concentration reached a maximum value of about 0.0023 mol/L at about 32 s, both NO and NO_2 concentrations started to decrease, and O_2 concentration continued to increase. When the experiment proceeded to about 52 s, the NO and NO_2 concentrations decreased to 0 mol/L, indicating that there were no NO and NO_2 in the gas cell, and the O_2 concentration also reached the maximum value of about 5.5×10^{-3} mol/L.

During the whole reaction process, the average measured temperature was 297.71 K, which did not show any obvious variation trend and was the same as the room temperature. The possible reason is that the total amount of reaction is too small; the average pressure was 1.03 atm, which was slightly higher than the ambient pressure. This was caused by the micropump continuously injecting O_3. The O_3 sensor at the gas outlet recorded data every 5 s. The O_3 sensor showed 0 mol/L from 0 to 35 s, indicating that no O_3 was discharged from the gas outlet, and the O_3 sensor started to display an indication greater than zero after 40 s. It indicated that more and more O_3 was discharged from the reaction gas cell. The variation of the experimental results is consistent with the effect of the molar ratio of O_3 to NO as well as the reaction products on the reaction process, demonstrating the accuracy of the spectroscopic measurement method for chemical reaction process measurements and the technical advantages of simultaneous measurements on multiple molecules and parameters. Based on the NO_x measurements, the variation in the denitrification rate of the reaction in the experiment was calculated, as shown in Fig. 3(g).

Further reaction kinetic analysis found that the NO + O_3 reaction rate is approximately 1.6 $\mu mol\,L^{-1}\,s^{-1}$, which exhibits nearly constant monotony and is mainly dependent on the feed rate of O_3. The NO_2 + O_3 reaction rate is low at the beginning and gradually increased to 1.4 $\mu mol\,L^{-1}\,s^{-1}$ around the stage of 30 s to 40 s, which is mainly limited by the NO_2 concentration. Both reactions of NO + O_3 and NO_2 + O_3 contribute to O_2 generation with a reaction rate approximately 2.8 $\mu mol\,L^{-1}\,s^{-1}$. The number of steps of the reaction is one, and the activation energy is about 3.09 kcal/mol. These data obtained using spectroscopic measurements can help to further investigate the chemical kinetic process of the chemical reaction, which is more beneficial to characterize the real proceeding process of the reaction compared to the traditional calculation or simulation methods.

4. Conclusion

In conclusion, the monitoring of the NO_x oxidation reaction process by laser WMS with a time interval of 0.1 s was performed to obtain the changes in gas temperature, pressure, NO, NO_2, and O_2 concentrations. Particularly, the measurement system is continuous, *in-situ*, and non-invasive. At the same time, the denitrification rate with the continuous injection of O_3 at different molar ratios of O_3 to NO was calculated, which verified the feasibility of laser molecular spectroscopy technology for chemical reaction measurement and technical advantages. However, in the current measurement, O_2 and NO_x are not measured by the same optical path due to the different wavelengths of the detector response, which may cause differences in the measurement results due to different gas diffusion paths; in addition, the time resolution of the current system is still relatively low, and the temperature resolution needs to be improved. These problems should be solved in future research by improved optical path design, optimized spectral pair selection, and increased tuning frequency to further develop the application of laser molecular spectroscopy for chemical reaction measurements.

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