

# Heterogeneous reaction of NO<sub>2</sub> with soot at different relative humidity

Chong Han<sup>1,2</sup> · Yongchun Liu<sup>1,3</sup> · Hong He<sup>1,3</sup>

Received: 23 February 2017 / Accepted: 12 July 2017 / Published online: 22 July 2017  
© Springer-Verlag GmbH Germany 2017

**Abstract** The influences of relative humidity (RH) on the heterogeneous reaction of NO<sub>2</sub> with soot were investigated by a coated wall flow tube reactor at ambient pressure. The initial uptake coefficient ( $\gamma_{\text{initial}}$ ) of NO<sub>2</sub> showed a significant decrease with increasing RH from 7 to 70%. The  $\gamma_{\text{initial}}$  on “fuel-rich” and “fuel-lean” soot at RH = 7% was  $(2.59 \pm 0.20) \times 10^{-5}$  and  $(5.92 \pm 0.34) \times 10^{-6}$ , respectively, and it decreased to  $(5.49 \pm 0.83) \times 10^{-6}$  and  $(7.16 \pm 0.73) \times 10^{-7}$  at RH = 70%, respectively. Nevertheless, the HONO yields were almost independent of RH, with average values of  $(72 \pm 3)\%$  for the fuel-rich soot and  $(60 \pm 2)\%$  for the fuel-lean soot. The Langmuir-Hinshelwood mechanism was used to demonstrate the negative role of RH in the heterogeneous uptake of NO<sub>2</sub> on soot. The species containing nitrogen formed on soot can undergo hydrolysis to produce carboxylic species or alcohols at high RH, accompanied by the release of little gas-phase HONO and NO.

**Keywords** Soot · NO<sub>2</sub> · HONO · Relative humidity · Competitive adsorption

Responsible editor: Gerhard Lammel

✉ Hong He  
honghe@rcees.ac.cn

<sup>1</sup> Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

<sup>2</sup> School of Metallurgy, Northeastern University, Shenyang 110819, China

<sup>3</sup> Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

## Introduction

Soot particles, which origin from the incomplete combustion of fossil and biomass fuels, are ubiquitous in the atmosphere. With an average emission inventory of 8–24 Tg of carbon per year, soot may account for ~10–15% of the total atmospheric aerosol mass (Penner and Eddleman 1993). Soot can provide a large specific surface area for the heterogeneous reactions, leading to changes in the atmospheric compositions by the chemical reactions of active species such as HO, O<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> (Ammann et al. 1998; Arens et al. 2001; Bertram et al. 2001; Gerecke et al. 1998; McCabe and Abbatt 2009; Khalizov et al. 2010; Kleffmann and Wiesen 2005; Lelièvre et al. 2004a, b; Saathoff et al. 2001; Salgado Muñoz and Rossi 2002; Stadler and Rossi 2000; Zhang and Zhang 2005). In particular, the chemical conversion of NO<sub>2</sub> to HONO on soot has attracted extensive attention as a possible source of HONO in the past years, thus affecting the oxidation capacity of the atmosphere.

Many studies have measured the uptake coefficient ( $\gamma$ ) of NO<sub>2</sub> and HONO yield on various soot including fuel combustion soot (*n*-hexane (Aubin and Abbatt 2007; Lelièvre et al. 2004b; Prince et al. 2002; Stadler and Rossi 2000), decane (Aubin and Abbatt 2007; Stadler and Rossi 2000), toluene (Kleffmann et al. 1999; Lelièvre et al. 2004b), and diesel (Kleffmann et al. 1999)), commercially available soot such as Degussa FW2 and Printex (Kleffmann et al. 1999), and spark discharge soot from graphite electrodes (Ammann et al. 1998; Kalberer et al. 1999a, b). The values of  $\gamma$  varied greatly from 10<sup>-1</sup> to 10<sup>-8</sup> as well as HONO yields were in a wide range of 0–100% (Ammann et al. 1998; Arens et al. 2001; Aubin and Abbatt 2007; Kalberer et al. 1999a; Khalizov et al.

2010; Kleffmann et al. 1999; Lelièvre et al. 2004b; Prince et al. 2002; Stadler and Rossi 2000), which may depend on the reaction conditions such as source of soot, structure and composition of soot, NO<sub>2</sub> concentration, and relative humidity (Prince et al. 2002).

The HONO generation from the reaction of NO<sub>2</sub> with H<sub>2</sub>O adsorbed on glass, Pyrex, and Teflon has been observed, suggesting a following possible reaction pathway (Finlayson-Pitts et al. 2003),



However, this mechanism is not applicable to the uptake of NO<sub>2</sub> on the soot surface, where HNO<sub>3</sub> was not detected as a product and the HONO yield was usually higher than 50%. This suggests that soot provides reactive surface sites for the HONO formation via a redox process (R2) (Kleffmann and Wiesen 2005; Stadler and Rossi 2000),



Soot contains various polar oxygen-containing functional groups such as C–O, C = O, OH, and COOH (Cain et al. 2010; Daly and Horn 2009; Han et al. 2012a, b), which may become the active adsorption sites of H<sub>2</sub>O. The adsorbed H<sub>2</sub>O may block some adsorptive or reactive sites of NO<sub>2</sub>, and thus decreasing the NO<sub>2</sub> uptake and HONO formation. As observed by Kalberer et al. (1999a), above the relative humidity of 40%, the HONO production decreased with increasing relative humidity due to competitive adsorption of H<sub>2</sub>O on the soot surface. Nevertheless, Kleffmann et al. (1999) found that the HONO yield increased continuously with increasing relative humidity, reaching an almost constant value of 50% at high relative humidity (>60%). In contrast, within the relative humidity range of 0–80%, Arens et al. (2001) reported that relative humidity cannot affect the formation of HONO. Therefore, the roles of H<sub>2</sub>O in the reaction of NO<sub>2</sub> to HONO on soot should be further investigated. In order to obtain reliable kinetic parameters, it is required to measure the reaction kinetics of NO<sub>2</sub> with soot at ambient relative humidity.

In this work, soot was produced by combusting *n*-hexane under controlled conditions. The uptake experiments of NO<sub>2</sub> on soot were performed using a flow tube reactor coupled to a NO<sub>x</sub> analyzer at ambient pressure. The uptake coefficients of NO<sub>2</sub> and HONO yields were measured as a function of relative humidity (RH). Langmuir-Hinshelwood mechanism was employed to explain the competition role of H<sub>2</sub>O in the NO<sub>2</sub> uptake on soot. The changes in the compositions of soot were analyzed by in situ attenuated total internal reflection infrared (ATR-IR) spectra. The role of RH in the release of HONO on the NO<sub>2</sub>-treated soot was also examined.

## Experimental sections

### Soot production

Soot samples were produced by combusting *n*-hexane (AR, Sinopharm Chemical Reagent Co., Ltd) in a co-flow diffusion burner as described in detail elsewhere (Han et al. 2012a, b). This burner basically consisted of a diffusion flame maintained by an airflow. The fuel was fed by a cotton wick extending into the liquid fuel reservoir. The airflow was a mixture of high purity O<sub>2</sub> and N<sub>2</sub>, and the volume ratio of O<sub>2</sub> to N<sub>2</sub> was exactly controlled by mass flow meters. The fuel/oxygen ratio was expressed as the molar ratio of the consumed fuel to the introduced oxygen during the combustion process. The samples produced at a relatively high fuel/oxygen ratio (0.18) were defined as “fuel-rich” soot, whereas the samples generated at a relatively low fuel/oxygen ratio (0.10) were defined as “fuel-lean” soot. At the burner exit, the collection of soot on the inner walls of a quartz tube was quickly completed within 20 s, which avoided a significant removal of organic carbon on soot due to the increase in the temperature of the tube. And then, the tube coated with soot was quickly transferred to the reactor, where a N<sub>2</sub> flow was introduced to avoid the aging of soot by the oxidizing species. With nitrogen Brunauer-Emmett-Teller (BET) physisorption analysis (Quantachrome Autosorb-1-C), the specific surface area of soot was measured to be 52.0 m<sup>2</sup>/g, which was used to calculate the mass-independent uptake coefficient.

### Flow tube reactor

The heterogeneous reaction of NO<sub>2</sub> with soot was performed in a horizontal cylindrical coated wall flow tube reactor at ambient pressure. The temperature was maintained at 298 K by circulating water through the outer jacket of the flow tube reactor (34 cm length and 1.6 cm inner diameter). The quartz tube (20 cm length, 1.0 cm inner diameter, and 1.4 cm outside diameter) coated with soot samples was located at the center of the reactor. NO<sub>2</sub> standard gas (50 ppmv in N<sub>2</sub>, Beijing Huayuan Gases Inc.) and high purity N<sub>2</sub> (99.99%, Beijing AP BEIFEN Gases Inc.) were used as received. With high purity N<sub>2</sub> as carrier gas, the total flow introduced into the reactor was 930 ml min<sup>-1</sup>, which ensured a laminar regime in the sample tube. NO<sub>2</sub> was introduced into the flow tube through a movable injector with 0.6 cm outside diameter, and its concentration was 160 ppb. During the reaction processes of NO<sub>2</sub> with soot, the NO<sub>2</sub> and NO concentrations were measured by a chemiluminescence analyzer (THERMO 42i). A quartz tube (10 cm length and 1.0 cm inner diameter) filled with 1.0 g Na<sub>2</sub>CO<sub>3</sub> was introduced to trap the formed HONO between the exit of the reactor and the analyzer, since HONO was also detected as NO<sub>2</sub> by the analyzer (Monge et al. 2010). NO and NO<sub>2</sub> together with HONO were detected using a

bypass tube, whereas only NO and NO<sub>2</sub> were measured using this Na<sub>2</sub>CO<sub>3</sub> tube. Thus, the HONO concentration was indirectly obtained as the difference of the NO<sub>2</sub> signal without and with the Na<sub>2</sub>CO<sub>3</sub> tube in the sampling line. RH was adjusted in the range of 7–70% by varying the ratio of dry N<sub>2</sub> to wet N<sub>2</sub>, and it was measured using a hygrometer (Center 314). The trapping efficiency of HONO by the Na<sub>2</sub>CO<sub>3</sub> tube was higher than 99% at different RH over 1.0 h for a 200 ppb HONO flow (Liu et al. 2015). The NO<sub>2</sub> uptake and HONO decomposition on the quartz tube were negligible during the control experiments. According to the detection limit (0.4 ppb) of the NO<sub>x</sub> analyzer, the systematic uncertainties of the NO<sub>2</sub> signal should be less than 7%, which depended on the concentrations of NO<sub>2</sub>.

### Uptake coefficient

The uptake behavior of NO<sub>2</sub> on soot can be described by a pseudo-first-order reaction (Monge et al. 2010). As shown in the following equation, the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) was proportional to the geometric uptake coefficient ( $\gamma$ ),

$$\frac{\ln(C_0/C_t)}{t} = k_{\text{obs}} = \frac{\gamma < c >}{2r_{\text{tube}}}, \quad (1)$$

where  $C_0$  and  $C_t$  are the NO<sub>2</sub> concentration at exposure time 0 and  $t$ , respectively;  $< c >$  and  $r_{\text{tube}}$  are the NO<sub>2</sub> average molecular velocity and the inner radius of sample tube, respectively. Since the diffusion of NO<sub>2</sub> into underlying layers of soot samples may happen,  $\gamma$  was a mass-dependent parameter and exhibited a linear increase in the soot mass range of 0.3–2.0 mg. Therefore, the mass-independent uptake coefficient ( $\gamma_{\text{BET}}$ ) was calculated using Eq. 2,

$$\gamma_{\text{BET}} = \frac{S_{\text{geom}} \times \gamma_{\text{geom}}}{S_{\text{BET}} \times m_{\text{soot}}}, \quad (2)$$

where  $S_{\text{geom}}$  is the geometric area of the quartz tube coated with soot,  $S_{\text{BET}}$  is the BET surface area of soot, and  $m_{\text{soot}}$  is the soot mass. The Cooney-Kim-Davis (CKD) method was used to correct the gas-phase diffusion limitations for  $\gamma_{\text{geom}}$  calculations (Cooney et al. 1974; Murphy and Fahey 1987), which has been widely described in previous studies (Monge et al. 2010; Ndour et al. 2009; Zelenay et al. 2011). According to Eqs. 1 and 2, initial uptake coefficients ( $\gamma_{\text{initial}}$ ) of NO<sub>2</sub> on soot were determined by averaging the NO<sub>2</sub> signal within the first 1.0 min during the reaction with soot, because the data was automatically recorded every minute by NO<sub>x</sub> analyzer.

### Analysis of soot surface compositions

The in situ attenuated total internal reflection infrared (ATR-IR) spectra during the reaction of NO<sub>2</sub> with soot were

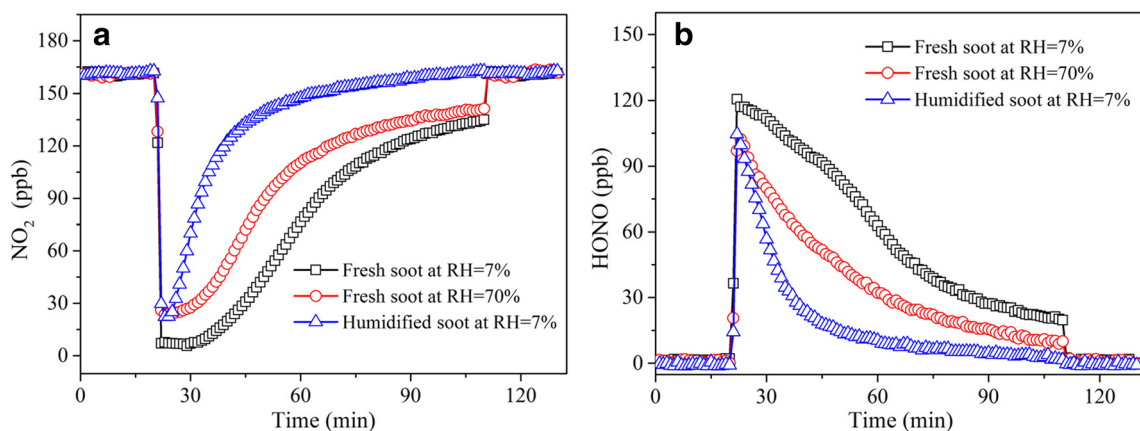
recorded using a Fourier transform infrared (FT-IR) spectrometer (NEXUS 6700). Soot produced by the *n*-hexane flame was directly deposited on the ZnSe crystal of the ATR-IR cell, which was sealed with quartz glass. Soot was purged by 100 ml min<sup>-1</sup> N<sub>2</sub> for 1 h at 298 K. Subsequently, a mixture of NO<sub>2</sub> and N<sub>2</sub> with a total flow rate of 100 ml min<sup>-1</sup> was introduced into ATR-IR cell. A high NO<sub>2</sub> concentration (5 ppm) was used to obtain better ATR-IR spectra signals. The spectra of soot were recorded (100 scans, 4 cm<sup>-1</sup> resolution) using the unreacted soot surface as reference. The experiments were performed at 298 K under ambient pressure.

## Results and discussion

### NO<sub>2</sub> uptake and HONO formation at different RH

Figure 1 shows the temporal changes of NO<sub>2</sub> and HONO concentrations in the reaction of NO<sub>2</sub> with soot. Upon exposure to soot, there was a clear time-dependent loss of NO<sub>2</sub> with a significant initial uptake (Fig. 1a). Due to the consumption of active sites, the deactivation of soot occurred quickly. When NO<sub>2</sub> was isolated from soot by moving the injector outside the reaction region, the NO<sub>2</sub> desorption was not observed, indicating that the reactive uptake should be the main contributor to the loss of NO<sub>2</sub>. Figure 1b shows that HONO was always released to the gas phase as long as NO<sub>2</sub> was consumed on soot. Moreover, coupled with initial NO<sub>2</sub> uptake, the HONO concentration reached the maximum value.

Soot surface has various oxygen-containing species such as ethers, ketones, lactones, and anhydrides (Cain et al. 2010; Daly and Horn 2009; Han et al. 2012a, b), which may become so-called primary adsorption centers to H<sub>2</sub>O. Uptake of H<sub>2</sub>O on soot has been observed by a Knudsen reactor connected with a mass spectrometer (Seisel et al. 2004). Therefore, H<sub>2</sub>O may have significant influences on the heterogeneous uptake reaction of NO<sub>2</sub> on soot. As shown in Fig. 1, compared to those at RH = 7%, NO<sub>2</sub> exhibited a lower initial uptake as well as HONO reached a lower maximum value at RH = 70%, remaining to continue over a following interval of tens of minutes. The integrated amounts of the lost NO<sub>2</sub> and the formed HONO within 90 min decreased from  $1.59 \times 10^{17}$  and  $1.21 \times 10^{17}$  molecules at RH = 7% to  $1.06 \times 10^{17}$  and  $8.05 \times 10^{16}$  molecules at RH = 70%, respectively. Based on BET area of soot, the number of NO<sub>2</sub> lost per unit specific soot surface area was calculated to decrease from  $3.06 \times 10^{14}$  molecules cm<sup>-2</sup> at RH = 7% to  $2.04 \times 10^{14}$  molecules cm<sup>-2</sup> at RH = 70% within 90 min. These values roughly corresponded to the number of surface reactive sites consumed per unit specific soot surface area. This confirms that H<sub>2</sub>O has negative effects on the NO<sub>2</sub> uptake and HONO formation on soot.



**Fig. 1** Temporal changes of NO<sub>2</sub> uptake (a) and HONO formation (b) on fresh “fuel-rich” soot at RH = 7% and 70% and humidified “fuel-rich” soot (soot was exposed to wet N<sub>2</sub> for 30 min at 25 °C) at RH = 7%

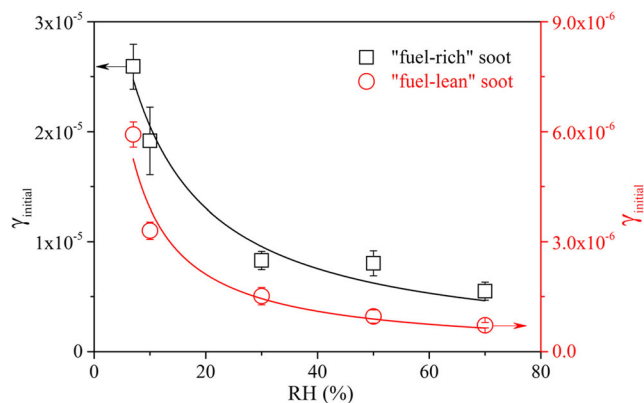
To further identify the negative role of H<sub>2</sub>O, a second set of experiments were performed in which soot that had been exposed to wet N<sub>2</sub> for 30 min was then exposed to NO<sub>2</sub> at RH = 7%. Compared to that on fresh soot at RH = 7%, NO<sub>2</sub> concentration on soot humidified by wet N<sub>2</sub> had a faster asymptotic recovery after the initial uptake, accompanied by a faster decrease of HONO concentration after reaching the maximum value. These results indicate that absorbed H<sub>2</sub>O leads to the decreases in the reactivity of soot toward NO<sub>2</sub>, which may be related to the restructuring of soot. Soot can collapse and become more compact due to pore condensation of H<sub>2</sub>O at high RH (Ma et al. 2013; Martin et al. 2013; Mikhailov et al. 2006), inhibiting the diffusion of NO<sub>2</sub> into the pore space of soot. Thus, some reactive sites available for NO<sub>2</sub> uptake and HONO formation on soot can be blocked by absorbed H<sub>2</sub>O.

Figure 2 shows the initial uptake coefficient ( $\gamma_{\text{initial}}$ ) of NO<sub>2</sub> on fresh soot as a function of RH. The errors represent the standard deviations based on three independent experiments. The  $\gamma_{\text{initial}}$  exhibited the inverse dependence on RH. The  $\gamma_{\text{initial}}$  on fuel-rich soot decreased from  $(2.59 \pm 0.20) \times 10^{-5}$  at RH = 7% to  $(5.49 \pm 0.83) \times 10^{-6}$  at RH = 70%. The  $\gamma_{\text{initial}}$  on fuel-lean soot decreased from  $(5.92 \pm 0.34) \times 10^{-6}$  to  $(7.16 \pm 0.73) \times 10^{-7}$  with increasing the RH from 7 to 70%. The decrease of  $\gamma_{\text{initial}}$  with RH can be ascribed to the competitive adsorption between H<sub>2</sub>O and NO<sub>2</sub> on soot. Popovicheva et al. (2008) found that the adsorbed H<sub>2</sub>O on soot continuously increased with RH from 0 to 70%. The  $\gamma_{\text{initial}}$  ( $3.6 \pm 2.0) \times 10^{-4}$  of H<sub>2</sub>O on soot was significantly larger than that of NO<sub>2</sub> as mentioned above (Seisel et al. 2004), meaning that the adsorption of H<sub>2</sub>O is preferred over NO<sub>2</sub>. This can well explain a decrease of  $\gamma_{\text{initial}}$  of NO<sub>2</sub> with RH. In addition, it was noticed that the reactivity of fuel-lean soot toward NO<sub>2</sub> was significantly lower than that of fuel-rich soot. It has been reported that the reactivity of soot toward NO<sub>2</sub> linearly depended on the contents of organic carbon in soot, which decreased with decreasing the fuel/oxygen ratio

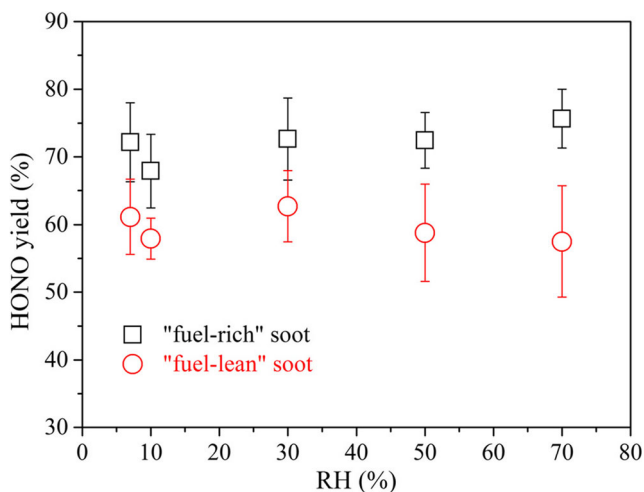
(Han et al. 2013b). As described in the “Experimental section”, N<sub>2</sub> was used as the carrier gas without O<sub>2</sub>. The composition of soot almost remained unchanged after the exposure to O<sub>2</sub> in the dark (Han et al. 2012b), suggesting that O<sub>2</sub> may have a slight effect on the uptake of NO<sub>2</sub> on soot. The values reported here should be the upper limit for the reaction of NO<sub>2</sub> with soot.

Figure 3 summarizes the HONO yield when NO<sub>2</sub> reacted with fresh soot at different RH. The HONO yield was defined as the ratio of integrated HONO formation amount to integrated NO<sub>2</sub> loss amount on soot. In the RH range of 7–70%, the HONO yields almost remained unchanged. The average HONO yield was  $(72 \pm 3)\%$  and  $(60 \pm 2)\%$  for fuel-rich and fuel-lean soot, respectively. This suggests that H<sub>2</sub>O is not limiting for the HONO generation on soot, since it may be already in large excess over the ppb NO<sub>2</sub> at low RH. In fact, the formation of HONO by the reaction of NO<sub>2</sub> with soot under dry conditions has been observed (Al-Abadleh and Grassian 2000; Aubin and Abbatt 2007; Lelièvre et al. 2004b; Stadler and Rossi 2000).

The average integrated HONO formation amount on fuel-rich soot at RH = 30–70% was calculated to be



**Fig. 2** Plots of  $\gamma_{\text{initial}}$  of NO<sub>2</sub> on fresh “fuel-rich” and “fuel-lean” soot versus RH. The black and red solid lines are the fitting curve using Eq. 10



**Fig. 3** Plots of the HONO yield on fresh “fuel-rich” and “fuel-lean” soot versus RH

$1.75 \times 10^{12}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$ . A typical aerosol surface concentration was reported to be  $10^3 \mu\text{m}^2 \text{cm}^{-3}$  in the urban atmosphere (Hueglin et al. 2005; Wehner and Wiedensohler 2003), and the mass of soot may reach an upper limit of 10–15% of the total atmospheric aerosols (Khalizov et al. 2010; Penner and Eddleman 1993). Thus, in the RH range of 30–70%, the formation rate of HONO by the reaction of  $\text{NO}_2$  with soot in aerosols was estimated to be 4–6 ppt  $\text{h}^{-1}$ . This value should be obviously larger than the average HONO formation rate in the typical atmospheric lifetime (several days) of soot, because the reaction kinetics of  $\text{NO}_2$  with soot quickly slowed down due to the consumption of the reactive sites on soot (Fig. 1a). Additionally, the  $\text{NO}_2$  concentration and the soot mass proportion used to determine the HONO formation rate were larger than the corresponding average atmospheric levels, which may cause an overestimation of the HONO formation rate.

### Langmuir-Hinshelwood mechanism analysis

Assuming that the uptake of  $\text{NO}_2$  on soot follows the Langmuir-Hinshelwood mechanism,  $\text{NO}_2$  is in rapid equilibrium between the gas phase and the soot surface, and the reaction takes place between the adsorbed species. If the surface reaction is the rate-limiting step, the pseudo-first-order reaction rate ( $v$ ) of  $\text{NO}_2$  can be written as:

$$-\frac{d[\text{NO}_2]_{\text{ads}}}{dt} = v = k_1[\text{NO}_2]_{\text{ads}} = k_1[S]_T\theta_{\text{NO}_2} \quad (3)$$

where  $t$  is the reaction time,  $[\text{NO}_2]_{\text{ads}}$  is the adsorbed  $\text{NO}_2$ ,  $k_1$  is the pseudo-first-order reaction rate coefficient,  $[S]_T$  is the total number of surface adsorption sites, and  $\theta_{\text{NO}_2}$  is the fraction of the sites occupied by  $\text{NO}_2$ . If the adsorption of  $\text{NO}_2$  on soot can be described by the

Langmuir isotherm,  $\theta_{\text{NO}_2}$  is given by Eq. 4 (Liu et al. 2015),

$$\theta_{\text{NO}_2} = \frac{K_{\text{NO}_2}[\text{NO}_2]_{\text{g}}}{1 + K_{\text{NO}_2}[\text{NO}_2]_{\text{g}} + K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]_{\text{g}}}, \quad (4)$$

where  $K_{\text{NO}_2}$  and  $K_{\text{H}_2\text{O}}$  are the Langmuir adsorption constant for  $\text{NO}_2$  and  $\text{H}_2\text{O}$ , respectively, and  $[\text{NO}_2]_{\text{g}}$  and  $[\text{H}_2\text{O}]_{\text{g}}$  are the concentrations of  $\text{NO}_2$  and  $\text{H}_2\text{O}$ , respectively. By substituting Eq. 4 into Eq. 3, the following equation is obtained:

$$v = \frac{k_1[S]_TK_{\text{NO}_2}[\text{NO}_2]_{\text{g}}}{1 + K_{\text{NO}_2}[\text{NO}_2]_{\text{g}} + K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]_{\text{g}}} \quad (5)$$

Thus, the pseudo-first-order rate coefficient is written as:

$$k_{1,\text{NO}_2} = \frac{k_1[S]_TK_{\text{NO}_2}}{1 + K_{\text{NO}_2}[\text{NO}_2]_{\text{g}} + K_{\text{H}_2\text{O}}[\text{H}_2\text{O}]_{\text{g}}} \quad (6)$$

By inserting Eq. 7 and Eq. 8 into Eq. 6,

$$k_{1,\text{NO}_2} = \frac{\gamma\langle c_{\text{NO}_2} \rangle}{2r_{\text{tube}}} \quad (7)$$

$$[\text{H}_2\text{O}] = \frac{P_{\text{H}_2\text{O}}^0[\text{RH}]}{RT} \quad (8)$$

The dependence of  $\gamma$  on RH can be described by Eq. 9,

$$\gamma = \frac{(2r_{\text{tube}}/\langle c_{\text{NO}_2} \rangle)k_1[S]_TK_{\text{NO}_2}}{1 + K_{\text{NO}_2}[\text{NO}_2]_{\text{g}} + \frac{K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^0[\text{RH}]}{RT}} \quad (9)$$

Because the uptake experiments were performed at a constant  $\text{NO}_2$  concentration, Eq. 9 can be simplified to Eq. 10,

$$\gamma = \frac{a}{b + c[\text{RH}]}, \quad (10)$$

where  $a = (2r_{\text{tube}}/\langle c_{\text{NO}_2} \rangle)k_1[S]_TK_{\text{NO}_2}$ ,  $b = 1 + K_{\text{NO}_2}[\text{NO}_2]_{\text{g}}$ , and  $c = \frac{K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}^0}{RT}$ . As shown in Fig. 2, the data of  $\gamma_{\text{initial}}$  as a function of RH was fitted using Eq. 10. The well-fitting results suggest that the Langmuir-Hinshelwood mechanism can satisfactorily describe the effects of RH on the uptake coefficients. The resulting equation for fuel-rich and fuel-lean soot is Eqs. 11 and 12, respectively.

$$\gamma_{\text{initial}} = \frac{1.87 \times 10^{-4}}{3.92 + 0.52[\text{RH}]} \quad (11)$$

$$\gamma_{\text{initial}} = \frac{6.57 \times 10^{-5}}{2.48 + 1.43[\text{RH}]} \quad (12)$$

According to Eqs. 11 and 12, the  $\gamma_{\text{initial}}$  for fuel-rich and fuel-lean soot at RH = 0% was extrapolated to be  $4.77 \times 10^{-5}$

and  $2.65 \times 10^{-5}$ , respectively. The  $\gamma_{\text{initial}}$  value at RH = 0% in this work was close to the reported values of  $\gamma_{\text{initial}}$ , from  $3.9 \times 10^{-5}$  to  $5 \times 10^{-5}$  for NO<sub>2</sub> on hexane soot under dry conditions (Al-Abadleh and Grassian 2000; Aubin and Abbatt 2007). The typical RH generally varied at 20–90% in the troposphere. As found in this work, the  $\gamma_{\text{initial}}$  of NO<sub>2</sub> on soot decreased with increasing RH. Thus, the  $\gamma_{\text{initial}}$  measured under dry conditions should result in an overestimated uptake ability of soot toward NO<sub>2</sub>. It should be pointed out that the NO<sub>2</sub> uptake coefficients would decrease as the active sites on soot were continuously consumed with exposure time. Soot may be also aged by various processes in the atmosphere such as the oxidation and the coating with organics, which may affect the kinetics of NO<sub>2</sub> on soot at different RH.

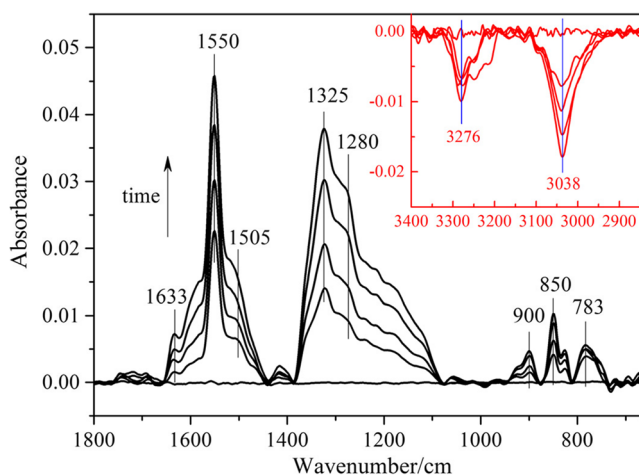
**Hydrolysis of species containing nitrogen formed on soot**

Besides gaseous HONO, surface species containing nitrogen have been confirmed during the heterogeneous reaction of NO<sub>2</sub> with soot (Akhter et al. 1984; Han et al. 2013a; Kirchner et al. 2000). The in situ ATR-IR spectra were used to investigate the temporal changes in the functional groups of soot. The unreacted soot surface was taken as the reference background spectrum. To obtain better IR signal, ATR-IR spectra of soot were recorded at a higher NO<sub>2</sub> concentration (5 ppm). N<sub>2</sub>O<sub>4</sub> may be involved in the reactions at high NO<sub>2</sub> concentrations. According to Akhter et al. (1984) and Sosedova et al. (2011), the equilibrium between NO<sub>2</sub>(g) and NO<sub>2</sub>(ads)/N<sub>2</sub>O<sub>4</sub>(ads) was first built before the reaction with soot. The pseudo-first-order rate coefficient at 5 ppm NO<sub>2</sub> will be orders of magnitude smaller than that at 160 ppb NO<sub>2</sub>, whereas there are similar products in the reactions of soot with 160 ppb NO<sub>2</sub> and 5 ppm NO<sub>2</sub> (Han et al. 2013a).

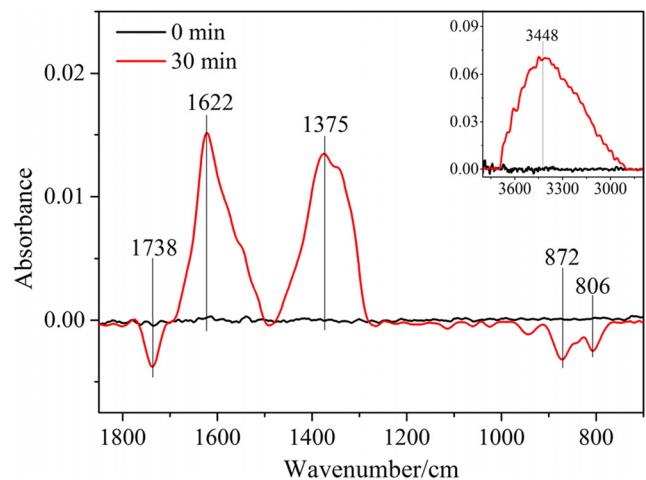
As shown in Fig. 4, ATR-IR spectra exhibited significant changes during the reaction of soot with NO<sub>2</sub>. The intensities

of peaks at 1633, 1550, 1505, 1325, 1280, 900, 850, and 783 cm<sup>-1</sup> increased with the time. The peaks at 1633 and 1280 cm<sup>-1</sup> were attributed to R-ONO (Akhter et al. 1984; Al-Abadleh and Grassian 2000; Kirchner et al. 2000). Two peaks at 1550 and 1325 cm<sup>-1</sup> were ascribed to aliphatic R-NO<sub>2</sub>, while the band around 1505 cm<sup>-1</sup> was assigned to aromatic Ar-NO<sub>2</sub> (Akhter et al. 1984; Al-Abadleh and Grassian 2000; Kirchner et al. 2000). Three peaks at 900, 850, and 783 cm<sup>-1</sup> were related to R-ONO<sub>2</sub>/R-ONO (Al-Abadleh and Grassian 2000). These results suggest that the species containing nitrogen were formed on the soot surface, which can be a reason of the fact that the HONO yield is always less than 100% (Fig. 3). In addition, the intensities of two bands at 3276 and 3038 cm<sup>-1</sup> obviously decreased, which was related to the consumption of alkyne and aromatic C-H, respectively.

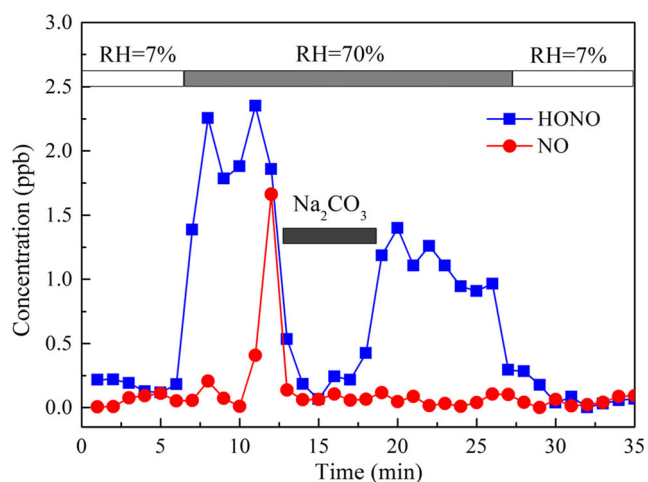
The soot aged by NO<sub>2</sub> (5 ppm) was exposed to a constant relative dry N<sub>2</sub> flow (RH = 7%) to promote desorption of species from the soot surface. Once the changes of ATR-IR spectra was not observed, the aged soot was exposed to a wet N<sub>2</sub> flow (RH = 70%). The aged soot was taken as the reference background spectrum. Figure 5 shows the changes of ATR-IR spectra when soot aged by NO<sub>2</sub> was exposed to wet N<sub>2</sub> at 30 min. Two negative peaks at 872 and 806 cm<sup>-1</sup> resulted from the decrease of R-ONO<sub>2</sub>/R-ONO (Al-Abadleh and Grassian 2000), confirming the hydrolysis of species containing nitrogen. The peak at 1375 cm<sup>-1</sup> was assigned to carboxylic species or alcohols, which resulted from the hydrolysis of lactone or anhydride species, as described by the negative peak at 1738 cm<sup>-1</sup> (Daly and Horn 2009). The OH in H<sub>2</sub>O was also detected at 1622 and 3448 cm<sup>-1</sup>, suggesting the presence of H<sub>2</sub>O adsorbed on the soot surface. It was noticeable that the hydrolysis of species containing nitrogen should lead to negative peaks in the region of 1650–1200 cm<sup>-1</sup> in ATR-IR spectra. However, this was not



**Fig. 4** Temporal changes of in situ ATR-IR spectra of “fuel-rich” soot during the reaction with NO<sub>2</sub> (5 ppm) at RH = 7%. The illustration in the upper right corner is the IR spectra in the range of 3400–2800 cm<sup>-1</sup>



**Fig. 5** IR spectra of “fuel-rich” soot aged by NO<sub>2</sub> (5 ppm) after being exposed to wet N<sub>2</sub> flow (RH = 70%). The illustration in the upper right corner is the IR spectra in the range of 3800–2800 cm<sup>-1</sup>



**Fig. 6** Gaseous products during the exposure of “fuel-rich” soot aged by  $\text{NO}_2$  (160 ppb) to the  $\text{N}_2$  flow at RH = 7 or 70%

observed due to the offset caused by the adsorption peaks of  $\text{H}_2\text{O}$  and carboxylic species or alcohols.

To determine whether high RH plays an enhancement role in the release of HONO on aged soot by  $\text{NO}_2$  (160 ppb), the surface of  $\text{NO}_2$ -aged soot was first purged by a relative dry  $\text{N}_2$  (7% RH). When the  $\text{NO}_2$  and NO concentrations were constant, a wet  $\text{N}_2$  flow (70% RH) was introduced. As shown in Fig. 6, the red circles and blue grids represented the NO and  $\text{NO}_2$  signals, respectively. When the carbonate tube was switched into the sampling line, it was proved that the  $\text{NO}_2$  signal should be ascribed to HONO. The formation of NO had a delay and only persisted for 1–2 min. Upon exposing the aged soot to wet  $\text{N}_2$ , HONO was continuously generated. According to Fig. 5, HONO may originate from the hydrolysis of species containing nitrogen on soot. It has been reported that the hydrolysis of organic nitrites (RONO) can produce HONO (Allen 1953; Iglesias and Casado 2002). On the other hand, that  $\text{H}_2\text{O}$  can occupy adsorptive sites at high RH, leading to the release of adsorbed HONO produced by the reaction of  $\text{NO}_2$  with soot, which should be a more reasonable explanation (Syomin and Finlayson-Pitts 2003). Figure 6 displays that the integrated HONO amount was about  $7 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$ , which was two orders of magnitude less than that from the direct reaction of  $\text{NO}_2$  with soot (Fig. 1). Therefore, the HONO yield within first 90 min range at RH = 70% seemed to be unchanged in comparison with that at lower RH (Fig. 2b). It should be noticed that if this HONO release can be always observed over a longer time scale, its integral amount may result in an increase of overall HONO yield.

## Conclusions

The  $\gamma_{\text{initial}}$  of  $\text{NO}_2$  on soot exhibited a significant decrease at RH = 7–70%. For fuel-rich and fuel-lean soot, the  $\gamma_{\text{initial}}$  at RH = 7% was  $(2.59 \pm 0.20) \times 10^{-5}$  and  $(5.92 \pm 0.34) \times 10^{-6}$ ,

respectively, while the corresponding one was  $(5.49 \pm 0.83) \times 10^{-6}$  and  $(7.16 \pm 0.73) \times 10^{-7}$  at RH = 70%, respectively. The HONO yield remained unchanged as RH increased, and its average value was  $(72 \pm 3)\%$  and  $(60 \pm 2)\%$  for fuel-rich and fuel-lean soot, respectively. The Langmuir-Hinshelwood mechanism can explain the negative influence of an increasing RH on  $\gamma_{\text{initial}}$ , which was ascribed to the competitive adsorption of  $\text{H}_2\text{O}$  on soot. On the basis of in situ ATR-IR spectra, the reaction of  $\text{NO}_2$  with soot produced various species containing nitrogen on soot including R-ONO, R- $\text{NO}_2$ , and R- $\text{ONO}_2$ , with the consumption of alkyne and aromatic compounds. The hydrolysis of species containing nitrogen may occur at high RH, followed by the generation of carboxylic species or alcohols and the release of little HONO and NO.

**Acknowledgements** This research was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05010301) and National Natural Science Foundation of China (21407020, 21190054, 91543109).

## References

- Akhter MS, Chughtai AR, Smith DM (1984) Reaction of hexane soot with  $\text{NO}_2/\text{N}_2\text{O}_4$ . *J Phys Chem* 88:5334–5342
- Al-Abadleh HA, Grassian VH (2000) Heterogeneous reaction of  $\text{NO}_2$  on hexane soot: a Knudsen cell and FT-IR study. *J Phys Chem A* 104: 11926–11933
- Allen AD (1953) Hydrolysis of organic nitrites. *Nature* 172:301–302
- Ammann M, Kalberer M, Jost DT, Tobler L, Rössler E, Piguet D, Gäggeler HW, Baltensperger U (1998) Heterogeneous production of nitrous acid on soot in polluted air masses. *Nature* 395:157–160
- Arens F, Gutzwiller L, Baltensperger U, Gäggeler HW, Ammann M (2001) Heterogeneous reaction of  $\text{NO}_2$  on diesel soot particles. *Environ Sci Technol* 35:2191–2199
- Aubin DG, Abbatt JPD (2007) Interaction of  $\text{NO}_2$  with hydrocarbon soot: focus on HONO yield, surface modification, and mechanism. *J Phys Chem A* 111:6263–6273
- Bertram AK, Ivanov AV, Hunter M, Molina LT, Molina MJ (2001) The reaction probability of OH on organic surfaces of tropospheric interest. *J Phys Chem A* 105:9415–9421
- Cain JP, Gassman PL, Wang H, Laskin A (2010) Micro-FTIR study of soot chemical composition—evidence of aliphatic hydrocarbons on nascent soot surfaces. *Phys Chem Chem Phys* 12:5206–5218
- Cooney DO, Kim SS, Davis EJ (1974) Analyses of mass transfer in hemodialyzers for laminar blood flow and homogeneous dialysate. *Chem Eng Sci* 29:1731–1738
- Daly HM, Horn AB (2009) Heterogeneous chemistry of toluene, kerosene and diesel soots. *Phys Chem Chem Phys* 11:1069–1076
- Finlayson-Pitts BJ, Wingen LM, Sumner AL, Syomin D, Ramazan KA (2003) The heterogeneous hydrolysis of  $\text{NO}_2$  in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism. *Phys Chem Chem Phys* 5:223–242
- Gerecke A, Thielmann A, Gutzwiller L, Rossi MJ (1998) The chemical kinetics of HONO formation resulting from heterogeneous interaction of  $\text{NO}_2$  with flame soot. *Geophys Res Lett* 25:2453–2456
- Han C, Liu Y, Liu C, Ma J, He H (2012a) Influence of combustion conditions on hydrophilic properties and microstructure of flame soot. *J Phys Chem A* 116:4129–4136

- Han C, Liu Y, Ma J, He H (2012b) Key role of organic carbon in the sunlight-enhanced atmospheric aging of soot by O<sub>2</sub>. *Proc Natl Acad Sci U S A* 109:21250–21255
- Han C, Liu Y, He H (2013a) Heterogeneous photochemical aging of soot by NO<sub>2</sub> under simulated sunlight. *Atmos Environ* 64:270–276
- Han C, Liu Y, He H (2013b) Role of organic carbon in heterogeneous reaction of NO<sub>2</sub> with soot. *Environ Sci Technol* 47:3174–3181
- Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H (2005) Chemical characterisation of PM<sub>2.5</sub>, PM<sub>10</sub> and coarse particles at urban, near-city and rural sites in Switzerland. *Atmos Environ* 39:637–651
- Iglesias E, Casado J (2002) Mechanisms of hydrolysis and nitrosation reactions of alkyl nitrites in various media. *Int Rev Phys Chem* 21:37–74
- Kalberer M, Ammann M, Arens F, Gäggeler HW, Baltensperger U (1999a) Heterogeneous formation of nitrous acid (HONO) on soot aerosol particles. *J Geophys Res Atmos* 104:13825–13832
- Kalberer M, Ammann M, Gäggeler HW, Baltensperger U (1999b) Adsorption of NO<sub>2</sub> on carbon aerosol particles in the low ppb range. *Atmos Environ* 33:2815–2822
- Khalizov AF, Cruz-Quinones M, Zhang R (2010) Heterogeneous reaction of NO<sub>2</sub> on fresh and coated soot surfaces. *J Phys Chem A* 114:7516–7524
- Kirchner U, Scheer V, Vogt R (2000) FTIR spectroscopic investigation of the mechanism and kinetics of the heterogeneous reactions of NO<sub>2</sub> and HNO<sub>3</sub> with soot. *J Phys Chem A* 104:8908–8915
- Kleffmann J, Wiesen P (2005) Heterogeneous conversion of NO<sub>2</sub> and NO on HNO<sub>3</sub> treated soot surfaces: atmospheric implications. *Atmos Chem Phys* 5:77–83
- Kleffmann J, Becker KH, Lackhoff M, Wiesen P (1999) Heterogeneous conversion of NO<sub>2</sub> on carbonaceous surfaces. *Phys Chem Chem Phys* 1:5443–5450
- Lelièvre S, Bedjanian Y, Pouvesle N, Delfau JL, Vovelle C, Bras GL (2004a) Heterogeneous reaction of ozone with hydrocarbon flame soot. *Phys Chem Chem Phys* 6:1181–1191
- Lelièvre S, Bedjanian Y, Laverdet G, Bras GL (2004b) Heterogeneous reaction of NO<sub>2</sub> with hydrocarbon flame soot. *J Phys Chem A* 108:10807–10817
- Liu Y, Han C, Ma J, Bao X, He H (2015) Influence of relative humidity on heterogeneous kinetics of NO<sub>2</sub> on kaolin and hematite. *Phys Chem Chem Phys* 17:19424–19431
- Ma X, Zangmeister CD, Gigault J, Mulholland GW, Zachariah MR (2013) Soot aggregate restructuring during water processing. *J Aerosol Sci* 66:209–219
- Martin M, Tritscher T, Jurányi Z, Heringa MF, Sierau B, Weingartner E, Chirico R, Gysel M, Prévôt ASH, Baltensperger U, Lohmann U (2013) Hygroscopic properties of fresh and aged wood burning particles. *J Aerosol Sci* 56:15–29
- McCabe J, Abbatt JPD (2009) Heterogeneous loss of gas-phase ozone on n-hexane soot surfaces: similar kinetics to loss on other chemically unsaturated solid surfaces. *J Phys Chem C* 113:2120–2127
- Mikhailov EF, Vlasenko SS, Podgorny IA, Ramanathan V, Corrigan CE (2006) Optical properties of soot-water drop agglomerates: an experimental study. *J Geophys Res Atmos* 111:D07209
- Monge ME, D'Anna B, Mazri L, Giroir-Fendler A, Ammann M, Donaldson DJ, George C (2010) Light changes the atmospheric reactivity of soot. *Proc Natl Acad Sci U S A* 107:6605–6609
- Murphy DM, Fahey DW (1987) Mathematical treatment of the wall loss of a trace species in denuder and catalytic converter tubes. *Anal Chem* 59:2753–2759
- Ndour M, Nicolas M, D'Anna B, Ka O, George C (2009) Photoreactivity of NO<sub>2</sub> on mineral dusts originating from different locations of the Sahara desert. *Phys Chem Chem Phys* 11:1312–1319
- Penner JE, Eddleman H (1993) Towards the development of a global inventory for black carbon emissions. *Atmos Environ* 27:1277–1295
- Popovicheva O, Persiantseva NM, Shonija NK, DeMott P, Koehler K, Petters M, Kreidenweis S, Tishkova V, Demirdjian B, Suzanne J (2008) Water interaction with hydrophobic and hydrophilic soot particles. *Phys Chem Chem Phys* 10:2332–2344
- Prince AP, Wade JL, Grassian VH, Kleiber PD, Young MA (2002) Heterogeneous reactions of soot aerosols with nitrogen dioxide and nitric acid: atmospheric chamber and Knudsen cell studies. *Atmos Environ* 36:5729–5740
- Saathoff H, Naumann KH, Riemer N, Kamm S, Möhler O, Schurath U, Vogel H, Vogel B (2001) The loss of NO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>3</sub>/N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>/HOONO<sub>2</sub> on soot aerosol: a chamber and modeling study. *Geophys Res Lett* 28:1957–1960
- Salgado Muñoz MS, Rossi MJ (2002) Heterogeneous reactions of HNO<sub>3</sub> with flame soot generated under different combustion conditions. Reaction mechanism and kinetics. *Phys Chem Chem Phys* 4:5110–5118
- Seisel S, Lian Y, Keil T, Trukhin ME, Zellner R (2004) Kinetics of the interaction of water vapour with mineral dust and soot surfaces at T=298 K. *Phys Chem Chem Phys* 6:1926–1932
- Sosedova Y, Rouvière A, Bartels-Rausch T, Ammann M (2011) UVA/Vis-induced nitrous acid formation on polyphenolic films exposed to gaseous NO<sub>2</sub>. *Photochem Photobiol Sci* 10:1680–1690
- Stadler D, Rossi MJ (2000) The reactivity of NO<sub>2</sub> and HONO on flame soot at ambient temperature: the influence of combustion conditions. *Phys Chem Chem Phys* 2:5420–5429
- Syomin DA, Finlayson-Pitts BJ (2003) HONO decomposition on borosilicate glass surfaces: implications for environmental chamber studies and field experiments. *Phys Chem Chem Phys* 5:5236–5242
- Wehner B, Wiedensohler A (2003) Long term measurements of submicrometer urban aerosols: statistical analysis for correlations with meteorological conditions and trace gases. *Atmos Chem Phys* 3:867–879
- Zelenay V, Monge ME, D'Anna B, George C, Styler SA, Huthwelker T, Ammann M (2011) Increased steady state uptake of ozone on soot due to UV/Vis radiation. *J Geophys Res Atmos* 116:D11301
- Zhang D, Zhang R (2005) Laboratory investigation of heterogeneous interaction of sulfuric acid with soot. *Environ Sci Technol* 39:5722–5728