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# Assessing indoor gas phase oxidation capacity through real-time measurements of HONO and NO<sub>x</sub> in Guangzhou, China

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The hydroxyl radical (OH) is one of the most important oxidants controlling the oxidation capacity of the indoor atmosphere. One of the main OH sources indoors is the photolysis of nitrous acid (HONO). In this study, real-time measurements of HONO, nitrogen oxides (NO<sub>x</sub>) and ozone (O<sub>3</sub>) in an indoor environment in Guangzhou, China, were performed under two different conditions: (1) in the absence of any human activity and (2) in the presence of cooking. The maximum NO<sub>x</sub> and HONO levels drastically increased from 15 and 4 ppb in the absence of human activity to 135 and 40 ppb during the cooking event, respectively. The photon flux was determined for the sunlit room, which has a closed south-east oriented window. The photon flux was used to estimate the photolysis rate constants of NO<sub>2</sub>,  $J(\text{NO}_2)$ , and HONO,  $J(\text{HONO})$ , which span the range between  $8 \times 10^{-5}$  and  $1.5 \times 10^{-5} \text{ s}^{-1}$  in the morning from 9:30 to 11:45, and  $8.5 \times 10^{-4}$  and  $1.5 \times 10^{-4} \text{ s}^{-1}$  at noon, respectively. The OH concentrations calculated by photostationary state (PSS) approach, observed around noon, are very similar, *i.e.*,  $2.4 \times 10$  and  $3.1 \times 10 \text{ cm}^{-3}$  in the absence of human activity and during cooking, respectively. These results suggest that under “high NO<sub>x</sub>” conditions (NO<sub>x</sub> higher than a few ppb) and with direct sunlight in the room, the NO<sub>x</sub> and HONO chemistry would be similar, independent of the geographic location of the indoor environment, which facilitates future modeling studies focused on indoor gas phase oxidation capacity.

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## Introduction

A comprehensive understanding of oxidant levels and that of their precursors in indoor atmosphere is of great importance, considering their effects on the health of inhabitants. To understand the quality of air that we breathe on a daily basis, scientists have been intrigued by research on primary pollution sources and sinks in indoor environments.<sup>1</sup> Combustion processes (cooking, heating the residence, *etc.*) comprise one of the most important pollution sources in the indoor environment, especially in some Asian countries like China.<sup>2,3</sup> Nitrous acid (HONO) and nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) represent an important class of indoor pollutants emerging from combustion processes. The importance of

HONO arises from its well-known health impacts, *e.g.*, lowering of human lung functionality<sup>4,5</sup> and converting to different carcinogenic species, such as nitrosamines.<sup>6–8</sup> The importance of HONO has been further emphasized by observations of high HONO levels indoors<sup>9–18</sup> and its role as a precursor of the highly reactive hydroxyl radicals (OH) in the indoor air.<sup>17</sup> Nitrogen dioxide (NO<sub>2</sub>) is a precursor of HONO through heterogeneous hydrolysis reactions and light-induced heterogeneous reactions occurring on various indoor surfaces.<sup>19–26</sup>

The contribution of HONO to the total OH budget in an indoor environment during the day was underestimated for a long time and has therefore been neglected in many models.<sup>27,28</sup> The first direct measurements of OH in indoor air<sup>17</sup> have shown that photolysis of HONO dominates the production of OH when the room is exposed to direct sunlight. Indeed, the UV fraction of sunlight can penetrate through windows and initiate the photochemical production of OH.<sup>17,18,29–31</sup> The effects of light emitted by indoor artificial lighting (LED, halogen lamps, fluorescent lamps) on potential photochemistry is still under discussion,<sup>32,33</sup> although it has been shown that renoxification can occur on paint surfaces upon irradiation with indoor lighting.<sup>34</sup> Emission of HONO is much more pronounced when the indoor walls painted by photocatalytic paints are irradiated by direct sunlight in the presence of NO<sub>2</sub>.<sup>25,26</sup> Knowledge about the formation of OH on an hour-to-hour and season-to-season basis at different geographic locations is of paramount importance to developing more accurate models<sup>35</sup> describing the secondary chemistry in the indoor environment.<sup>3,28,36–42</sup>

Indoor HONO was first identified and measured by James Pitts and coworkers using differential optical absorption spectroscopy (DOAS).<sup>43</sup> Since then, several studies have attempted to measure indoor HONO levels by indirect techniques (denuders, passive samplers, *etc.*).<sup>14,15,18,44</sup> However, measuring NO<sub>x</sub> and HONO at the same time represents an experimental challenge due to the possible sampling artefacts and chemical interference during the measurements.<sup>45,46</sup>

For example, observations by Spicer *et al.* (2001)<sup>47</sup> demonstrated that nitrous acid represents a quantitative interference to NO<sub>2</sub> measurements by three different passive sampling techniques. In this study, real-time measurements of NO, NO<sub>2</sub>, HONO, and O<sub>3</sub> were performed in an indoor environment to better characterize their mixing ratios, sources, and sinks under two different scenarios: (1) in the absence of any human activity and (2) in the presence of cooking. This study is the first campaign in China and worldwide employing the long path absorption photometer (LOPAP) for real-time measurements of HONO<sup>48,49</sup> in an indoor environment. We also measure spectral irradiance from sunlight penetrating through the windows into the room and determine the photolysis rates of HONO and NO<sub>2</sub> under different conditions. The photolysis rates of HONO and measured mixing ratios of NO, NO<sub>2</sub> and HONO are used to estimate OH concentrations by pseudo stationary state (PSS) approach and to compare the estimated OH concentrations under different conditions.

## Methods summary

The experimental campaign was performed in the period 01–15 December in a lab room of the following dimensions: 3.7 m (length) × 2.2 m (width) × 2.8 m (height), situated at Jinan University, Guangzhou, China (Fig. S1†). There was one window with dimensions 1.1 m × 0.9 m. The lab room was oriented south-east. CO<sub>2</sub> was added as dilution tracer through the main door before the background experiments in order to measure the air exchange rates. During the cooking scenario, the decay of CO<sub>2</sub> released by the gas stove was monitored to estimate the air exchange rate. Two fans were installed in the corners to ensure air homogeneity in the lab room. Each set of measurements (in the absence of human activity and in the presence of cooking) during different periods of the day was repeated at least twice. The combustion appliance consists of a natural gas stove. Peanut oil was used for the cooking experiments. The cooking experiments lasted about 15 to 20 min. The cooking scenario in this lab room can be compared with cooking in a typical residence without using a fume hood.

All the instruments were placed in the neighbouring room (Fig. S1†). NO<sub>x</sub>, O<sub>3</sub> and CO<sub>2</sub> were sampled by Teflon tubes with *ca.* 2 m length going through a hole made in the wall to the lab room at 2 m distance from the gas stove and 1 m from the flat collector of the spectroradiometer. For HONO measurements, the sampling port was placed directly in the lab room nearby the flat collector of the spectroradiometer and at 2 m distance from the gas stove. To prevent clogging of the instrument, a cyclone aerosol size selector was installed prior to the sampling port to remove the coarse particles. A Teflon tube about 40 cm long was connected between the cyclone aerosol size selector and the sampling port.

It has to be noted that the VOC composition and mixing ratios of the oxidants (NO<sub>x</sub>, O<sub>3</sub>) depend on both indoor and outdoor sources. The OH concentration depends strongly on the actinic flux and, hence, the orientation of the room, the solar zenith angle, and the thickness and nature of the windows glass.<sup>29</sup> Therefore, the values of the measured NO<sub>x</sub>, O<sub>3</sub> and HONO mixing ratios correspond to this particular indoor environment.

## Real-time instruments

Online instruments were used for time-resolved measurements of HONO, NO, NO<sub>2</sub>, O<sub>3</sub>, VOCs, carbon dioxide (CO<sub>2</sub>), relative humidity (RH), and temperature (*T*). For HONO measurements, LOPAP (QUAMA, Germany), was used, for which the operational procedure is described in detail elsewhere.<sup>48,49</sup> Briefly, HONO is sampled in a stripping coil by a fast chemical reaction and converted into an azo dye, which is photometrically detected by long path absorption in a special Teflon tubing (Teflon AF2400).

During all the experiments, the detection limit was smaller than 30 parts per trillion (ppt), with a total accuracy of ±10% and measured time response of about 5 min under the operation conditions applied (gas flow and pump flow of 1 l min<sup>-1</sup> and 500 ml min<sup>-1</sup>, respectively).

The mixing ratios of NO<sub>x</sub>, NO<sub>2</sub> and NO were simultaneously measured by a chemiluminescence instrument (CLD 88p, Eco Physics, Switzerland) coupled to a photolytic (metal halide lamp) converter (PLC 860, Eco Physics, Switzerland). The NO<sub>x</sub> analyzer is very sensitive, with a detection limit of 110 ppt. The photolytic converters have about 10% interference against HONO.<sup>50</sup> Conservatively, it is suggested that a positive bias of up to 1 ppb in the accuracy of the measurements may have been possible, which falls in the range of the stated 10% uncertainty.

The mixing ratios of O<sub>3</sub> were measured by calibrated ozone analyzer (Thermo Scientific Model 49i, USA). The detection limit of this O<sub>3</sub> analyzer is 0.5 ppb, with a time resolution of 20 s. The CO<sub>2</sub> decay was monitored online by time-of-flight single-photon ionization mass spectrometry, (TOF-SPIMS; SPIMS 3000, Hexin Analytical Instrument Co., Ltd., China) with a time resolution of one second. Polydimethylsiloxane (PDMS, thickness 0.002 int, Technical Products Inc, USA) membrane was used in the injector of the TOF-MS. A vacuum ultraviolet (VUV) light generated by a commercial D2 lamp (Hamamatsu, Japan) was used for ionization of the molecules. Single-photon ionization, with 10.8 eV energy of the single photon, is capable of performing the “soft” ionization of the detected organic compound.

The ToF mass analyzer consists of a double pulsed acceleration region, a field-free drift tube, a reflector and an ion detector. This TOF-MS has a LOD of approximately 1 ppb for most of the trace gases.<sup>51</sup> The average air exchange rate calculated from the decay of CO<sub>2</sub> was *ca.* 0.6 h<sup>-1</sup>, in agreement with previous studies focused on observations in residences.<sup>18,52–54</sup> For example, the air exchange rate during a five-day period in a residence situated in Toronto, Canada, varied in a range between 0.19 and 0.74 h<sup>-1</sup>, with an average value of 0.5 h<sup>-1</sup>.<sup>53</sup> Zhou *et al.* (2019)<sup>54</sup> estimated a mean air exchange rate of 0.69 (±0.30) h<sup>-1</sup> during cooking events in an occupied home at Syracuse, New York.

## Results and discussion

### Spectral irradiance and photolysis rates of NO<sub>2</sub> and HONO

The variation of sunlight intensity during the day, at different latitudes and seasons, is an important parameter because it can alter the chemistry of various indoor environments. This is due to the fact that photochemistry plays an important role in the formation of free radicals such as OH.<sup>29–31,36</sup> The spectral irradiance was measured during different periods of the day (Fig. 1). Photon fluxes were estimated from spectral irradiance following a conversion procedure described elsewhere to calculate *J* values of HONO and NO<sub>2</sub>.<sup>17</sup> Certainly, the conversion procedure will affect the calculations of *J* values of HONO and NO<sub>2</sub>, performed thereafter. The variation of the determined actinic flux during the direct irradiation of the room in the period between 9:30 a.m. and 12:15 p.m. on December 3<sup>rd</sup> is shown in Fig. 1. For comparison, the spectral actinic fluxes calculated with the tropospheric ultraviolet and visible (TUV) model (TUV version 5.3)<sup>55</sup> are also shown for outdoors with cloudless conditions at 12:15 p.m. on December 3<sup>rd</sup>.

Fig. 1 shows that the closed glass window filters out the wavelengths below 330 nm, but still, an important fraction of

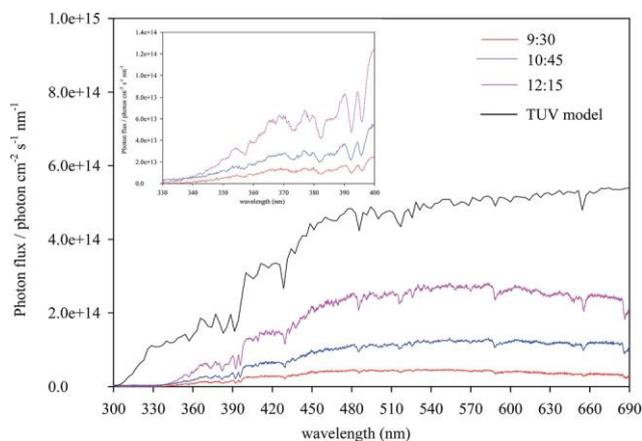


Fig. 1 Comparison of indoor actinic fluxes measured in direct sunlight in the lab room with the outdoor solar actinic flux determined by the TUV model. The TUV actinic flux is determined for Guangzhou (latitude 23.12899, longitude 113.12899), solar zenith angle (SZA) of 56.10° on December 3<sup>rd</sup>, at 12:15 p.m. The inset shows the indoor actinic fluxes in the UV range (330 nm < λ < 400 nm).

UV light (330 nm < λ < 400 nm) penetrates indoors, which can allow the photochemistry to occur. The determined actinic flux from the sunlight penetrating indoors was used to calculate the first-order photolysis rate constants of HONO, *J*(HONO), and NO<sub>2</sub>, *J*(NO<sub>2</sub>).<sup>56</sup>

$$J \approx \int_{\lambda=340\text{nm}}^{\infty} F \sigma(\lambda) f(\lambda) d\lambda; \quad (1)$$

where *F* is the actinic flux summed over the wavelength interval Δλ (photons cm<sup>-2</sup> s<sup>-1</sup>), *J* is the photolysis rate constant (s<sup>-1</sup>), σ(λ) (cm<sup>2</sup>) is the absorption cross-section, and *f*(λ) (dimensionless) is the photolysis quantum yield of either NO<sub>2</sub> or HONO.

The sum in eqn (1) is performed from the lower limit of wavelengths available in this indoor environment, λ<sub>0</sub> ≈ 330 nm, to a certain wavelength λ<sub>1</sub> at which either the primary quantum yield or the absorption cross section of either HONO or NO<sub>2</sub> becomes negligible. The recommended values of the quantum yields for NO<sub>2</sub> photolysis and absorption cross sections were used for the calculations of *J*(NO<sub>2</sub>).<sup>57</sup>

Indeed, HONO photolysis occurs at wavelengths 300 nm < λ < 405 nm.<sup>58</sup> As the wavelengths between 330 and 405 nm are readily transmitted indoors,<sup>17,18,29–31</sup> the HONO photolysis produces OH radicals as follows:



The recommended absorption cross sections for the *J*(HONO) calculations were used.<sup>57</sup> Measuring the quantum yields for R1 represents an experimental challenge because of contamination of the HONO by other strongly absorbing species, like NO<sub>2</sub>, requiring corrections for their contributions to the absorption.<sup>56</sup> It is usually assumed, for a maximum photolysis, that the quantum yield for R1 is 1 at λ < 400 nm.<sup>59</sup>

The photolysis rate constants of NO<sub>2</sub> and HONO calculated from the measured spectral irradiance in direct sunlight in the lab room are shown in Fig. 2.

The asymmetric time-dependence of  $J(\text{HONO})$  and  $J(\text{NO}_2)$  values can be partly explained by the change in the incidence angle of the sunlight and the reflection of sunlight from indoor surfaces after 12:00 leading to higher light transmission. Indeed, the higher SZA leads to increased intensity of reflected light from the indoor walls.<sup>29</sup> In the morning, between 9:30 and 11:45, the room was irradiated with sunlight intensity that yields an average  $J(\text{HONO})$  of  $1.5 \times 10^{-5} \text{ s}^{-1}$  and  $J(\text{NO}_2)$  of  $8 \times 10^{-5} \text{ s}^{-1}$ . However, at noon, the  $J(\text{HONO})$  and  $J(\text{NO}_2)$  values peaked at  $1.5 \times 10^{-4} \text{ s}^{-1}$  and  $8.5 \times 10^{-4} \text{ s}^{-1}$ , respectively. These values are in excellent agreement with the peak values of  $J(\text{HONO})$   $\approx 1.5 \times 10^{-4} \text{ s}^{-1}$  and  $J(\text{NO}_2)$   $\approx 8 \times 10^{-4} \text{ s}^{-1}$  recorded on 21/07/2011 in a classroom in Marseille, France,<sup>17</sup> although the classroom was exposed to direct sunlight in the evening (17:00–19:00), and also in agreement with  $J(\text{HONO})$   $\approx 7.2 \times 10^{-5} \text{ s}^{-1}$  and  $J(\text{NO}_2)$   $\approx 8.5 \times 10^{-4} \text{ s}^{-1}$  determined for a sunlit region (around noon) in a residence in New York.<sup>18</sup> Gandolfo *et al.* (2016)<sup>29</sup> used a 2p spectral radiometer to measure the spectrally resolved actinic flux in a room situated in Marseille, France, during summer and winter periods. These authors measured a maximum  $J(\text{HONO})$   $\approx 1.7 \times 10^{-4} \text{ s}^{-1}$  during the summer period and  $J(\text{HONO})$   $\approx 1.4 \times 10^{-4} \text{ s}^{-1}$  during the wintertime, in a sunlit room. The maximum value observed for  $J(\text{NO}_2)$  in direct sunlight was  $1.4 \times 10^{-3} \text{ s}^{-1}$  during summertime and  $1.2 \times 10^{-3} \text{ s}^{-1}$  during wintertime. Both the  $J(\text{HONO})$  and  $J(\text{NO}_2)$  values measured during the winter and summer period are very similar with the corresponding values in this study, demonstrating that in sunlit regions of the room, the photolysis rate constants of HONO and NO<sub>2</sub> exhibit similar values independent of the season and geographic location. This is an important outcome of this study with respect to future modelling studies of indoor air photochemistry, in particular, regarding the modelling of OH radical chemistry.

These  $J(\text{HONO})$  and  $J(\text{NO}_2)$  values are smaller compared to the outdoor photolysis rate constants of HONO and NO<sub>2</sub> (*e.g.*, near the closed window, with up to 50% of outdoor sunlight<sup>29</sup>). For example, the mean values of  $J(\text{HONO})$  and  $J(\text{NO}_2)$

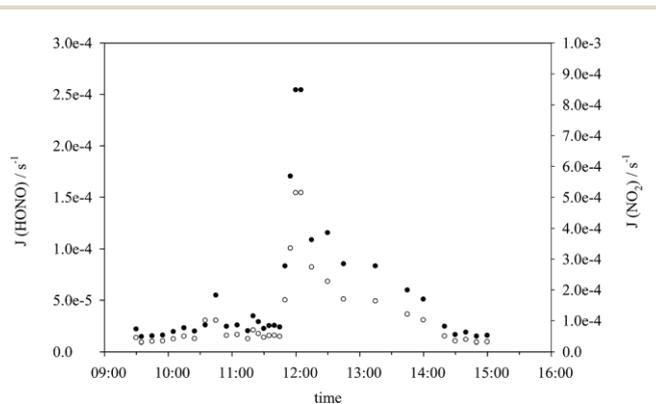


Fig. 2 The photolysis rate constants of HONO (●) and NO<sub>2</sub> (○) in the period between 9:30 a.m. and 3 p.m. on December 3<sup>rd</sup>, in the lab room in Guangzhou.

determined for the day period between 12:00 and 16:00 during the summer in a rural site of Guangzhou were  $1.2 \times 10^{-3}$  and  $6.6 \times 10^{-3} \text{ s}^{-1}$ , respectively.<sup>60</sup> The peak values of  $J(\text{HONO})$  and  $J(\text{NO}_2)$  during that same campaign were  $1.8 \times 10^{-3}$  and  $1 \times 10^{-2} \text{ s}^{-1}$ . A similar peak value of  $J(\text{HONO})$   $\approx 1.6 \times 10^{-3} \text{ s}^{-1}$  was observed during the Berlioz campaign near Berlin, Germany.<sup>61</sup> Peak values of  $J(\text{NO}_2)$  reached  $1 \times 10^{-2}$  and  $8 \times 10^{-3} \text{ s}^{-1}$  during the field campaigns in Santiago de Chile, Chile,<sup>62</sup> and Thessaloniki, Greece,<sup>63</sup> respectively. Although the maximum indoor values of  $J(\text{HONO})$  and  $J(\text{NO}_2)$  are smaller in comparison to the corresponding outdoor values, they induce photochemical reactions and OH production in the sunlit indoor environment (*vide infra*).

In the afternoon, between 14:00 and 15:00, the mean  $J(\text{HONO})$  and  $J(\text{NO}_2)$  again dropped to  $1.9 \times 10^{-5}$  and to  $1 \times 10^{-4} \text{ s}^{-1}$ , respectively, as was the case in the morning—indicating that photochemistry can be operational during the long period of the day (from 9:00 to 15:00) in this particular indoor environment.

HONO, NO<sub>x</sub> and O<sub>3</sub> mixing ratios in the absence of human activity and during the cooking event

During the cooking event, peaks of HONO and NO<sub>2</sub> of about 40 ppb and 133 ppb were detected, respectively (Fig. 3).

The observed HONO values during the cooking activity are much higher compared to previous studies that used passive samplers, which have very poor time resolution (days to weeks) and cannot detect the huge variations that occur due to the combustion process. For example, Leaderer *et al.*<sup>64</sup> reported HONO levels of about 5 ppb, observed during the winter in houses with gas ranges in Albuquerque, New Mexico. The average indoor HONO concentration measured by passive sampler was 4.6 ppb in the presence of a gas range in Southern California homes.<sup>14</sup>

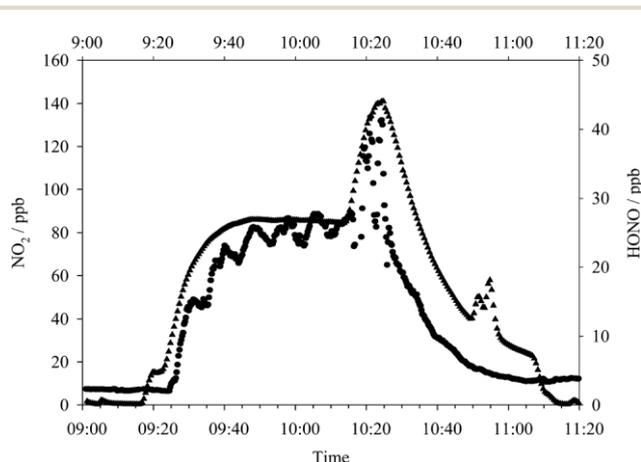


Fig. 3 The mixing ratios of (●) HONO and (○) NO<sub>2</sub> during a cooking event at December 07 2018 in the lab room on the campus at JNU, Guangzhou, China. The combustion started with  $\frac{1}{2}$  flame at 9:17. At 10:20, the knob of the gas appliance was turned to the maximum. The sharp increase of both NO<sub>2</sub> and HONO mixing ratios at 10 : 20 correspond to the increased combustion regime (maximum gas flame) of the gas appliance.

The average HONO mixing ratio during daytime and in the absence of any human activity was in the range between 3 and 4 ppb (see, *e.g.*, Fig. S3†). This value agrees with the HONO levels measured at similar indoor conditions. Recently, Zhou *et al.* (2018)<sup>18</sup> reported an indoor background HONO mixing ratio of  $4.0 \pm 2.5$  ppb in an occupied home at Syracuse, New York. Average HONO levels of about 5 ppb were also detected in a classroom in Marseille at ambient conditions when extra NO<sub>2</sub> was not added in the classroom.<sup>17</sup> A mean HONO value of 5.3 ppb was observed in a residence situated in Toronto, Canada.<sup>53</sup> Collins *et al.* (2018)<sup>53</sup> have shown that indoor surfaces play an important role as a source and sink of HONO, impacting its balance. Indeed, NO<sub>2</sub> is a precursor of HONO through dark and light-induced heterogeneous reactions with indoor surfaces.<sup>19,20,22–25,65</sup> In this study, the average background NO<sub>2</sub> mixing ratio in the lab room in Guangzhou was 12.4 ppb (Fig. S3†), which is higher than the background NO<sub>2</sub> mixing ratio (2 ppb) measured at the house in Syracuse, New York<sup>18</sup> and lower than the mean background NO<sub>2</sub> level (30 ppb) measured in the classroom in Marseille.<sup>17</sup> In the absence of *in situ* sources, the indoor NO<sub>2</sub> level strongly depends on the outdoor NO<sub>2</sub>, which can infiltrate indoors through the ventilation. For example, the lab room is located in a building at the campus of JNU far away from the main road, while the classroom in Marseille was located in a building on the main road with frequent vehicular traffic. During the cooking event, the NO<sub>2</sub> mixing ratio greatly increased, peaking at 133 ppb (Fig. 3), which is much higher than the previously reported NO<sub>2</sub> values in the presence of cooking (30 ppb)<sup>54</sup> and other combustion sources (17.3 ppb,<sup>18</sup> 52 ppb<sup>14</sup>). To our best knowledge, the reason for the small fluctuations of NO<sub>2</sub> in the period between 9:40 and 10:20 is not known (Fig. 3). The NO mixing ratios during the cooking activity rose to 180 ppb, while Zhou *et al.*<sup>18</sup> reported a NO peak of about 113 ppb during the cooking. However, Zhou *et al.* (2019)<sup>54</sup> reported a NO peak value of about 180 ppb during the cooking event in a residence near New York.

The ratio between HONO and NO<sub>2</sub> is an important indicator of the heterogeneous NO<sub>2</sub> → HONO conversion on indoor surfaces.<sup>14,19–22</sup> In this study, the average HONO/NO<sub>2</sub> background scenario is 0.36, which is higher than the HONO/NO<sub>2</sub> ratio of 0.17 and 0.08 measured in Californian homes and in Albuquerque residences, respectively.<sup>12,14</sup> This value of 0.36 is also higher than the HONO/NO<sub>2</sub> ratio of 0.13, which was recently observed in a residence in Toronto at RH (36–40%).<sup>53</sup> A very high mean ratio of 1.4 averaged over both events (background scenario and cooking) was recently observed in a residence in New York, indicating that HONO represents a significant fraction of the oxidized nitrogen burden in that residence.<sup>18</sup> When oxidant concentrations decreased to background conditions, the HONO/NO<sub>2</sub> ratio doubled to 2.2, indicating secondary chemical sources of HONO in that particular residence in New York.<sup>18</sup> Previous studies reported HONO/NO<sub>2</sub> ratios in the range between 0.1 and 0.3 (ref. 14–16 and 64) in residences with electric ranges, gas ranges and gas stoves. During the cooking event, we did not consider the HONO/NO<sub>2</sub> ratio, as HONO and NO<sub>2</sub> are directly emitted by the combustion

process; hence, total HONO cannot be entirely considered as a product formed during the heterogeneous reaction of NO<sub>2</sub> with indoor surfaces.

The mixing ratios of another important indoor oxidant, ozone (O<sub>3</sub>),<sup>66</sup> were at sub-ppb levels in the duration of the campaign except the ventilation periods, when O<sub>3</sub> was penetrating indoors from outside. Under the conditions considered in this study, O<sub>3</sub> does not play a role as an oxidant; hence, NO<sub>2</sub>, HONO, and OH are the key players in this particular indoor environment. This is also in agreement with some very recent measurements of O<sub>3</sub> mixing ratios in residences in North America.<sup>18,53</sup> O<sub>3</sub> mixing ratios were less than 10 ppb in a residence in Toronto, which was lower than or similar to outdoor O<sub>3</sub> values. In a residence in New York, the O<sub>3</sub> mixing ratios were at sub-ppb levels for the entire campaign except during periods of significant infiltration of outdoor air. These measurements indicate that O<sub>3</sub> is a less important oxidant indoors than previously thought. Arguably, O<sub>3</sub> could be adsorbed on various indoor surfaces and play a role in heterogeneous reactions;<sup>41,66</sup> however, its presence in the gas phase was negligible during the recent measurements in residences in North America<sup>18,53</sup> and in this study. Future O<sub>3</sub> measurements in different dwellings are necessary to confirm or disprove this hypothesis.

#### Pseudo photostationary state (PSS) model

The pseudo photostationary state (PSS) model can be used to estimate the OH concentrations at NO<sub>x</sub> levels higher than a few hundred ppts.<sup>17,62,67</sup> Since, in this study, the measured NO<sub>x</sub> levels in both scenarios (in the absence and presence of cooking) were in the order of tens of ppbs, the secondary OH production can be balanced with the secondary OH loss.<sup>17,62,67–71</sup> In other words, the RO<sub>2</sub> and HO<sub>2</sub> initiators should not be considered as net OH sources because the consumption of OH through the reactions with VOCs (OH + VOCs) is balanced by the OH produced through HO<sub>2</sub> recycling (HO<sub>2</sub> + NO) without a significant additional secondary OH production. As a result of the balance between secondary OH production and elimination, the total rates of OH initiation and loss can be estimated by considering only the net OH sources and sinks implemented in the PSS model (*vide infra* eqn (4)). The excellent agreement between the OH concentrations modelled by comprehensive master chemical mechanism (MCM) and PSS approach during both seasons, winter and summer, in Santiago de Chile<sup>67</sup> confirms that the PSS model can reasonably explain the OH concentrations in an indoor environment with high NO<sub>x</sub> levels. Hence, the PSS approach seems to be an appropriate tool to model the OH concentrations in the lab room under the experimental conditions in this study. Performing a detailed master chemical mechanism (MCM) model<sup>72</sup> is beyond the scope of this study, but it is recommended for future studies. In the PSS model, the primary OH sources are balanced with the OH sinks,  $P_{\text{OH}}(\text{prim}) \approx P_{\text{OH}}(\text{loss})$ . The primary OH production rate  $P_{\text{OH}}(\text{prim})$  is given as follows:

$$P_{\text{OH(prim)}} \approx J(\text{HONO})[\text{HONO}] + J(\text{O}^1\text{D})[\text{O}_3]F_{\text{OH}} + k_{\text{O}_3+\text{alkene}}[\text{alkene}][\text{O}_3]F_{\text{OH}_2} \quad (2)$$

where  $J(\text{HONO})$  ( $\text{s}^{-1}$ ) is the photolysis first-order rate constant of HONO,  $[\text{HONO}]$  (molecules per  $\text{cm}^3$ ) is the concentration of HONO,  $J(\text{O}^1\text{D})$  ( $\text{s}^{-1}$ ) is the photochemical formation rate constant of  $\text{O}^1\text{D}$  from  $\text{O}_3$  photolysis,  $[\text{O}_3]$  is the ozone concentration (molecules per  $\text{cm}^3$ ),  $F_{\text{OH}}$  is the yield of OH formation due to photolysis of ozone,  $k_{\text{O}_3+\text{alkene}}$  ( $\text{cm}^3$  per molecule per s) is the rate constant for the reaction between  $\text{O}_3$  and the corresponding alkene, and  $F_{\text{OH}_2}$  is the yield of OH formation due to ozonolysis of alkenes. The loss rate of OH can be presented as follows:

$$P_{\text{OH(loss)}} \approx k_{\text{OH}+\text{NO}}[\text{OH}][\text{NO}] + k_{\text{OH}+\text{NO}_2}[\text{OH}][\text{NO}_2] + k_{\text{OH}+\text{HONO}}[\text{OH}][\text{HONO}] / \text{molecules per cm}^3 \text{ per s}, \quad (3)$$

where  $k_{\text{OH}+\text{NO}}$ ,  $k_{\text{OH}+\text{NO}_2}$ , and  $k_{\text{OH}+\text{HONO}}$  ( $\text{cm}^3$  per molecule per s) are the rate constants for the reactions between OH and NO, OH and  $\text{NO}_2$ , and OH and HONO, respectively. Eqn (3) is valid under the assumption that the radical propagation by VOC oxidation is sufficiently fast ( $L(\text{OH})\text{VOCs} \approx P(\text{OH})\text{VOCs}$ ).<sup>62,67</sup>

As a result,  $\text{OH}_{\text{PSS}}$  can be estimated with the following equation:

$$\text{OH}_{\text{PSS}} \approx \frac{J(\text{HONO})[\text{HONO}] + J(\text{O}^1\text{D})[\text{O}_3]F_{\text{OH}} + k_{\text{O}_3+\text{alkene}}[\text{alkene}][\text{O}_3]F_{\text{OH}_2}}{k_{\text{OH}+\text{NO}}[\text{NO}] + k_{\text{OH}+\text{NO}_2}[\text{NO}_2] + k_{\text{OH}+\text{HONO}}[\text{HONO}]} \quad (4)$$

The  $J(\text{O}^1\text{D})$  due to ozone photolysis can be neglected, as the UV fraction of sunlight ( $\lambda < 320$  nm), which is responsible for the photodissociation of ozone, is filtered out by the glass window (Fig. 1). The photon flux emitted from the artificial light available in the lab room is also not sufficient to photolyse ozone (Fig. S1†), in agreement with Kowal *et al.*, 2018.<sup>31</sup> As the concentrations of ozone were also very low, at sub-ppb levels, the second and third term in eqn (4) can be neglected.

Finally, the PSS model described in eqn (4) becomes:

$$\text{OH}_{\text{PSS}} \approx \frac{J(\text{HONO})[\text{HONO}]}{k_{\text{OH}+\text{NO}}[\text{NO}] + k_{\text{OH}+\text{NO}_2}[\text{NO}_2] + k_{\text{OH}+\text{HONO}}[\text{HONO}]} \quad (5)$$

In this study, we applied eqn (5) to calculate the OH concentrations in the absence of human activity and during a cooking period. The obtained  $\text{OH}_{\text{PSS}}$  concentrations under both case scenarios are shown in Fig. 4.

The average daytime  $\text{OH}_{\text{PSS}}$  value at background scenario is  $3.7 \times 10^5 \text{ cm}^{-3}$ . Very similar averaged daytime values were obtained during the cooking activities *i.e.*,  $\text{OH}_{\text{PSS}} \approx 3.1 \times 10^5 \text{ cm}^{-3}$  and  $3.8 \times 10^5 \text{ cm}^{-3}$  for the cooking periods in the morning (10:15–10:30 and 11:45–12:00, respectively). However, high  $\text{OH}_{\text{PSS}}$  concentrations were observed around noon, spanning the range between  $1.4 \times 10^6 \text{ cm}^{-3}$  and  $3.1 \times 10^6 \text{ cm}^{-3}$  during the cooking events and  $2.4 \times 10^6 \text{ cm}^{-3}$  in the background

scenario, which are in excellent agreement with the directly measured peak OH concentrations of *ca.*  $2 \times 10^6 \text{ cm}^{-3}$  in a classroom in Marseille, France.<sup>17</sup> The cooking events carried out in the morning and noon periods only slightly influenced the peak OH concentrations compared to the background scenario. The most important parameter is the spectral irradiance of the sunlight that is transmitted through the windows. The peak OH concentrations formed through photolysis of HONO would largely depend on the spectral irradiance, the thickness of the glass windows, the solar zenith angle and the orientation of the room.<sup>29</sup>

There is excellent agreement between the maximum indoor  $\text{OH}_{\text{PSS}}$  concentrations in Guangzhou of  $3.1 \times 10^6 \text{ cm}^{-3}$  and the  $\text{OH}_{\text{PSS}}$  concentrations determined in the classroom in Marseille of  $1.8 \times 10^6 \text{ cm}^{-3}$  (ref. 17) due to the similar OH production rates. Indeed, for the background scenario (without human activity), the maximum OH production rate from this study of  $2.5 \times 10^7$  radicals  $\text{cm}^{-3} \text{ s}^{-1}$  is similar to the maximum OH production rate of  $2.9 \times 10^7$  radicals  $\text{cm}^{-3} \text{ s}^{-1}$  due to HONO photolysis, although the classroom in Marseille was northwest oriented, allowing direct sunlight in the room only in the evening (17:00–19:00).<sup>17</sup> The maximum OH production rate from this study of  $2.5 \times 10^7$  radicals  $\text{cm}^{-3} \text{ s}^{-1}$  for the background scenario is 3 times higher than the OH production rate of  $8.3 \times 10^6$  radicals  $\text{cm}^{-3} \text{ s}^{-1}$  calculated in the sunlit area of an

occupied home at Syracuse, New York.<sup>18</sup> This difference in the maximum OH production rates, with the same background HONO levels of a few ppbs, can be ascribed to the higher  $J(\text{HONO}) \approx 1.5 \times 10^{-4} \text{ s}^{-1}$  measured in direct sunlight in the indoor environment in Guangzhou compared to  $J(\text{HONO}) \approx 7.2 \times 10^{-5} \text{ s}^{-1}$  measured in a sunlit area in the home in Syracuse, New York.<sup>18</sup>

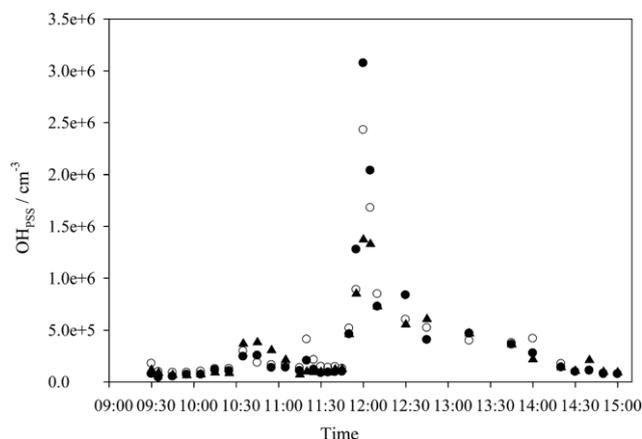


Fig. 4 The estimated  $\text{OH}_{\text{PSS}}$  concentrations in the room located on the campus of JNU, Guangzhou, China, (B) in the absence of human activity, (○) in the presence of cooking (10:15–10:30), and (▲) in the presence of cooking (11:45–12:00).

## Conclusions

The observed results from this study show that under “high NO<sub>x</sub>” conditions (NO<sub>x</sub> higher than a few ppb), OH could peak indoors at  $3.1 \times 10^6 \text{ cm}^{-3}$  for certain periods of the day when sunlight directly irradiates the room. This modelled OH value is similar to the directly measured peak OH values of  $1.8 \times 10^6 \text{ cm}^{-3}$  under “high NO<sub>x</sub>” conditions in the classroom in Marseille.<sup>17</sup>

This shows that in sunlit areas of a kitchen or a bedroom, the OH concentrations would reach identical peak values, which in turn are similar to the outdoor OH values. However, this is only valid if radical propagation by VOC oxidation is fast.<sup>62,67</sup> These results demonstrate that under “high NO<sub>x</sub>” conditions, the NO<sub>x</sub> and HONO chemistry would be pretty much similar, independent of the geographic location of the indoor environment. In addition, the similarity of the measured spectral irradiances in this indoor environment in China with some previous measurements in the EU<sup>17,29</sup> and US<sup>31</sup> is an important outcome of this study with respect to future modelling studies of indoor air photochemistry. The similar *J*(HONO) values is of particular importance regarding the modelling of OH radical chemistry. An important conclusion drawn from this work is that OH concentrations are very similar in the absence of human activity and in the presence of cooking. That is because both case scenarios are considered as “high NO<sub>x</sub>” conditions, which is always the case in residences. The sub ppb levels of NO<sub>x</sub> can only be detected in some administration buildings that are located far away from intense traffic and other combustion sources.

However, the combination of direct sunlight in the room and various combustion sources (candle, gas stove)<sup>18,73</sup> can lead to different OH concentrations depending on the orientation of the room, as well as the thickness and the nature of the glass windows. For this reason, further measurements of OH radical concentrations constrained with the MCM model, including the transport of species from indoor to outdoor and *vice versa*, are needed in order to obtain a clearer picture of indoor oxidation capacity in the presence of high NO<sub>x</sub> levels generated by various combustion processes (candle, gas range, gas plate, gas stove).

OH chemistry can induce the photochemical transformation of VOCs into highly oxidized organic molecules (HOMs)<sup>74</sup> and secondary organic aerosols (SOA) in various indoor environments and potentially affect human health.<sup>3</sup> The OH radicals are expected to be crucial not only for secondary organic aerosol growth but also to new particle formation.<sup>75</sup> Therefore, a comprehensive understanding of OH production under “high NO<sub>x</sub>” levels as well as HOMs/SOA on an hour-to-hour and season-to-season basis will be essential to developing more accurate models describing the gas-phase chemistry of indoor environments.

## Conflicts of interest

The authors declare no competing financial interests.

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