Research Article
Combining Chamber Experiments and Model Simulations to Evaluate an Indoor HONO Source with Surface Photochemical Properties

Youfeng Wang,1,2 Chong Zhang,1 Jianshu Wang,1 Yaru Wang,1 Yingjie Zhang,1,3 Weili Lin,4 and Chunxiang Ye1

1SKL-ESPC & SEPKL-AERM, College of Environmental Sciences and Engineering, and Center for Environment and Science, Peking University, Beijing 100871, China
2Beijing Municipal Ecological and Environmental Monitoring Center, Beijing, China
3School of Ecology and Nature Conservation, Beijing Forestry University, Beijing 100083, China
4College of Life and Environmental Sciences, Minzu University of China, Beijing, China

Correspondence should be addressed to Chunxiang Ye; c.ye@pku.edu.cn

Received 11 March 2023; Revised 5 September 2023; Accepted 8 September 2023; Published 6 October 2023

Nitrous acid (HONO) is an emerging indoor pollutant that can exert adverse health effects. The chemical production of indoor HONO has been attributed to NO2 heterogeneous reactions, and the source strength has been extensively evaluated via laboratory and model simulation studies. Photolysis of surface nitrate has recently been proposed as an indoor HONO source based on correlation analysis between indoor HONO accumulation and visible light radiation. However, neither experimental validation of the proposed mechanism nor source strength characterization is currently available. In this work, we designed an outdoor photochemical chamber (OPC) to simulate indoor HONO accumulation and established an indoor photochemical model (ICM) to calculate the indoor HONO budget. Indoor HONO accumulation revealed a distinct diel variation with a daytime maximum. Only with this indoor HONO source, the ICM reproduced the indoor HONO budget determined in the OPC. The enhanced reactive cross section of surface nitrate in visible light accounted for the major portion of the HONO source budget (77.2%) and the distinct diel variation. Success with the ICM encouraged us to simulate the HONO budget in real indoor environments. The calculated HONO production rates from surface nitrate photolysis at noon ranged from 1.4 to 4.1 ppbv h−1 under different indoor scenarios. On a daily average, this indoor HONO source contributed 42.4–52.7% to the total chemical sources in the living room but only contributed 4.7% to that in the kitchen, where NO2 heterogeneous reactions dominated.

1. Introduction

From air quality and human health perspectives, the indoor environment is worthy of much more research attention as a highly frequented living environment for residents [1]. Indoor air is influenced by outdoor air pollutant inputs and indoor sources and hence could notably differ from outdoor air [2]. Deep concern on indoor air quality led us to research areas involving indoor sources or indoor physical and chemical processes that control the distribution of both gaseous and particulate pollutants.

Compared to the outdoor atmosphere, the indoor environment features a high surface area to volume (S/V) ratio [3] and low ultraviolet (UV) radiation [4, 5]. As such, surface reactions of (semi)volatile organic and inorganic compounds have drawn intensive research attention [6–9]. Scientists have treated indoor surfaces as surface reservoirs containing chemical constituents subject to exchange with
the gas phase. Several groups have obtained measurements on the release of volatile organic compounds and nitrous acid (HONO) from indoor surfaces and have identified corresponding sources [10–12]. Adopting HONO as an example, the surface nitrite reservoir is 1–2 orders of magnitude more abundant than the indoor HONO [10]. Changes in room temperature or indoor HONO concentration can lead to a decrease in the surface nitrite reservoir and indoor HONO [10, 12]. The ultimate sources of HONO or surface nitrite include direct emissions from combustion processes and surface reactions. Burning candles, gas stoves, cigarette smoking, and open fireplaces [13] are presumably the major emission sources. A major indoor chemical source of HONO is associated with the photoenhanced heterogeneous reaction of NO2 on various indoor surfaces [14–17]. The HONO production from NO2 surface reactions and its response with the relative humidity (RH) have been consistently observed under indoor irradiation [14]. Knowledge of the relationship between HONO production rate and NO2 concentration under different light intensities (Table S1 and references therein [14, 15, 18–29]) facilitates the parameterization of the photoenhanced uptake coefficient of NO2 (γ, as expressed in equation (1) in kinetic models.

\[
\gamma = \gamma_0 \times EF. \quad (1)
\]

EF is the uptake enhancement factor under a defined light density relative to dark conditions (\(\gamma_0\)), which is vital for the evaluation of the HONO production from photoenhanced NO2 surface reactions.

A novel chemical source of indoor HONO in discussion is the photolysis of surface nitrate. Schwartz-Narbonne et al. measured HONO release employing several indoor lamps and proposed the photolysis of nitrate absorbed on painted walls as a novel indoor HONO source [30]. However, neither the detailed reaction mechanism nor the reaction rate has been examined. A similar proposal of enhanced nitrate photolysis on snow/ice surfaces has introduced the concept of a quasiliquid layer (QLL) on snow/ice surfaces, which allows the coexistence of quasi-liquid water, nitrate, and organic matter absorbed on surfaces [31]. Later, enhanced photolysis of nitrate on aerosol particle surfaces and other ambient surfaces, such as tree leaves, has also been confirmed in several laboratory studies, with a rate determined by the nitrate surface density [32–37]. Scientists have employed the concept of catalytic surface films and surface catalysis mechanisms to describe the dependence of the photolysis rate on the nitrate surface density or nitrate surface coverage [32–34, 37]. Although the microphysicochemical properties of the QLL and surface films have not been comprehensively and quantitatively characterized, they are analogous to a certain extent, namely, these films preserve nitrate in a similar but particular state far from being isolated, which might be the key reason for the catalyzed photolysis of surface nitrate [36–39]. Svoboda et al. calculated the absorption spectrum of bare nitrate anions and nitrate-water clusters, confirming a shift in the 300 nm absorption band depending on the number of water molecules [40]. In laboratory, researchers have also measured a redshift in the absorption spectra of nitrate on silicon surfaces [41, 42] and HNO3/NO3 on sapphire window surfaces [43], in the 290–365 nm range. Recently, we measured and reported the enhanced and redshifted reactive cross section of nitrate on aerosol particles with the enhanced absorption spectrum extending from 365 to 605 nm [44]. These measurements added key information on the surface catalysis mechanism, i.e., more overlap between the absorption spectrum of surface-absorbed nitrate and light spectrum could lead to increased HONO production via enhanced photolysis of surface nitrate powered by both UV and visible light under solar radiation or indoor lighting. It is likely that the contribution of longer wavelengths in UV or even visible light might cause indoor HONO accumulation. One reason is the increased HONO production beyond 300 nm as a result of the enhancement in both the absorption cross section and photon flux at longer wavelengths. Another reason is the dependence of HONO photolysis on UV light with wavelengths shorter than 400 nm [45], which is either mostly filtered by windows or not emitted by indoor lamps. Hence, the presumed consequence is enhanced production and suppressed photolysis loss leading to an inevitable accumulation of indoor HONO. With absorption cross section and photolysis rate available, our assumption can be quantitatively evaluated in a similar experiment to that of Schwartz-Narbonne et al. [30].

The indoor surface reactions producing HONO could be simplified as a two-step process, i.e., chemical production of nitrite on the surface, which is followed by partitioning and diffusion within the surface and bulk and gas phases. When the chemical production of nitrite dominates, partitioning and diffusion do not influence the immediate HONO yield resulting from photoenhanced NO2 heterogeneous reactions [14]. The HONO production from either the photolysis of surface-absorbed nitrate or photoenhanced NO2 heterogeneous reactions on aerosol particle surfaces highly depends on the light intensity [14, 34], suggesting a robust linkage between nitrite chemical production and the immediate HONO yield. Therefore, the HONO production rate, \(P_{HONO}\), as described in the fundamental photochemistry, can be defined in equation (2) as follows:

\[
P_{HONO} = \int N_{\gamma} \sigma(\lambda) \varnothing(\lambda) d\lambda, \quad (2)
\]

where \(N_{\gamma}\), \(\sigma(\lambda)\), and \(\varnothing(\lambda)\) denote the reactant pollutant (surface-absorbed nitrate) amount, light spectrum, absorption cross section or absorption spectrum of surface pollutants, and corresponding quantum yield of the photochemical product (HONO in this case), respectively. The surface-absorbed nitrate amount and actinic flux could be directly measured in the real indoor environment. To evaluate the indoor HONO production, the product of the absorption cross section of surface-absorbed nitrate and the corresponding quantum yield of HONO at each wavelength refers to our recent laboratory-determined reactive cross
section of surface-absorbed nitrate \([44]\), \(\sigma_{\text{rec}}(\lambda)\) (equation (3)), which can be obtained as follows:

\[ \sigma_{\text{rec}}(\lambda) = \sigma(\lambda)\varnothing(\lambda). \]  

With laboratory-determined \(\sigma_{\text{rec}}(\lambda)\), reasonable evaluation of this indoor HONO source is practical.

In this study, an outdoor photochemical chamber (OPC) with painted wall (Dulux latex paint) and regulating ventilation was built to simulate an enclosed room. HONO accumulation was directly monitored as a function of surface photochemical aging and illumination. An indoor photochemical model (ICM) summarizing surface-absorbed nitrate photolysis, photoenhanced \(\text{NO}_2\) heterogeneous reactions, and other HONO budget terms, i.e., HONO ventilation and photolysis losses, was constructed to simulate the HONO accumulation and budget in our OPC experiment. Reproduction of HONO accumulation in the OPC could facilitate further application of the ICM in the evaluation of this HONO source in real indoor environments. The environmental variation in this indoor HONO source was characterized with the surface nitrate density and window transmission of the actinic flux as major influencing factors.

2. Materials and Methods

2.1. Outdoor Photochemical Chamber (OPC) Experiment. The configuration of our OPC is shown in Figure S1, and the dimensions of the OPC are summarized in Table S2. The OPC comprised a stainless-steel-structured cubic reactor with a side length of 0.5 m and \(S/V\) ratio of 12 m\(^{-1}\). The chamber interior walls except for the roof were painted white (paint brand: Dulux) to simulate the painted wall surfaces in households, and the external walls were covered with thermal insulation materials and wood. The chamber roof consisted of a UV-cutoff glass filter to mimic indoor lighting conditions \([46]\). The glass filter provided a high transmittance of 89% at 500 nm with a cutoff wavelength of 425 nm (Figure S2). The OPC was equipped with a gas inlet system and a measurement system. The gas inlet system allowed flow control through a set of mass flow controllers and could deliver either ambient air, zero air, or laboratory mixing air into the chamber. A modified long-path absorption photometric (LPAP) instrument was used to measure the HONO and \(\text{NO}_2\) levels in the chamber at a total sampling rate of 0.8 L min\(^{-1}\). The measurement detection limits for HONO and \(\text{NO}_2\) reached 3 and 9 ppv, respectively, with a precision within 25% \([44]\).

Ventilation, surface properties, lighting conditions, and \(\text{NO}_2\) concentration are major influencing factors, and these parameters were therefore adopted as control factors in this OPC experiment. The OPC experiments were performed under a ventilation flow of 1.0 L min\(^{-1}\) (or a ventilation rate of ca. 0.48 h\(^{-1}\)) to maintain a slight positive pressure in the chamber and to prevent air permeation from the ambient air. Before each experiment, the dormant window was maintained open to allow air exchange, indoor aerosol particle deposition, and HNO\(_3\) partitioning. A chamber aged for half a year was used to simulate indoor wall surfaces. In the lighting control experiment, LED lamps, and solar radiation were compared. When LED lamps (5 W) were employed as light sources, the OPC chamber was placed in a dark environment, and HONO accumulation was monitored as the LED lamps were turned on or off. When solar radiation was employed as the light source, the OPC chamber was placed outdoors at the Peking University (PKU; 39.99°N, 116.30°E) site approximately 27 m above ground level. The solar spectrum and photolysis frequencies of HONO and \(\text{NO}_2\) were measured via a charge-coupled device (CCD) spectrometer (Figure S3). In \(\text{NO}_2\) concentration control design, parallel experiments with low- and high-\(\text{NO}_2\) input airflow were conducted. Low-\(\text{NO}_2\) air was generated by passing ambient air through glass tubes packed with potassium permanganate (KMnO\(_4\)) pellets and activated carbon, followed by a sodium carbonate (Na\(_2\)CO\(_3\)) denuder to remove reactive nitrogen species, including NO\(_x\), HONO, and HNO\(_3\). High-\(\text{NO}_2\) air was generated by passing ambient air through the Na\(_2\)CO\(_3\) denuder to remove only HONO and HNO\(_3\). In each experiment, the HONO and \(\text{NO}_2\) concentrations in the OPC and ambient air were simultaneously monitored.

2.2. Data Processing for the OPC Experiment. The HONO accumulation rate (in ppbv h\(^{-1}\)) resulting from surface nitrate photolysis in the OPC, \(d[HONO]_{\text{acc}}/dt\), can be obtained from measurements of the raw HONO accumulation rate, \(d[HONO]_{\text{indoor}}/dt\):

\[
\frac{d[HONO]_{\text{indoor}}}{dt} = \text{HONO source} - \text{HONO sink},
\]

\[\text{HONO source} = \frac{d[HONO]_{\text{acc}}}{dt} + \frac{d[HONO]_{\text{NO}_2}}{dt} + F_{\text{des}} S V,\]

\[\text{HONO sink} = \frac{d[HONO]_{\text{ph}}}{dt} + \frac{d[HONO]_{\text{vent}}}{dt} + F_{\text{ads}} S V,
\]

where \(d[HONO]_{\text{NO}_2}/dt\), \(d[HONO]_{\text{ph}}/dt\), and \(d[HONO]_{\text{vent}}/dt\) denote the source or sink strength of the photoenhanced heterogeneous reactions of \(\text{NO}_2\), HONO photolysis loss, and HONO ventilation loss, respectively, and \(F_{\text{des}}\) and \(F_{\text{ads}}\) are the HONO desorption and adsorption fluxes, respectively, representing the dynamic equilibrium between the surface nitrite reservoir and HONO.

\(d[HONO]_{\text{NO}_2}/dt\) is the first-order reaction involving the \(\text{NO}_2\) concentration and light intensity as primary kinetic assumptions, as expressed in

\[
\frac{d[HONO]_{\text{NO}_2}}{dt} = -\frac{1}{4} \times [\text{NO}_2] \times 3600 \times \omega(\text{NO}_2) \times \left(\frac{S - S_{\text{shining}}}{V} \times \gamma_0 + \frac{S_{\text{shining}}}{V} \times \gamma\right),
\]

where \(\omega(\text{NO}_2) = \sqrt{8RT/\pi M}\) is the thermal velocity of \(\text{NO}_2\), \(R\) is the ideal gas constant, \(T\) is the absolute temperature,
and $M$ is the molecular mass of NO$_2$. $S_{\text{shining}}$ denotes the sunlit area in the OPC, which is twice the dormant window surface area, i.e., 0.5 m$^2$. The dependence of EF (enhancement factor of $y$ relative to $y_0$) on the photolysis frequency of NO$_2$, $j_{\text{NO}_2}$, refers to the established linear relationship between EF and the light intensity [14, 20, 21, 25], as calculated with equation (8). EF is also dependent on the initial NO$_2$ concentration, much higher in low-NO$_x$ conditions than in high-NO$_x$ conditions [14, 20, 21]. Parameterization of $y_0$ and EF will be further discussed in Section 3.2.

$$y = y_0 \times EF = y_0 \times 6 \times \frac{j_{\text{NO}_2}}{j_{\text{NO}_2, \text{noontime}}}, \quad (8)$$

$d\left[HONO\right]_{\text{ph}}/dt$ can be determined via the HONO photolysis frequency, $j_{\text{HONO, indoor}}$, and a mixing ratio (equation (9)). $j_{\text{HONO, indoor}}$ can be calculated via an equation analogous to equation (2), as expressed in equation (10). The absorption cross-section of HONO and unit yield can be referred to the JPL dataset [47].

$$d\left[HONO\right]_{\text{ph}}/dt = j_{\text{HONO, indoor}} \times [\text{HONO}], \quad (9)$$

$$j_{\text{HONO, indoor}} = \int I(\lambda)_{\text{indoors}} \sigma_{\text{HONO}}(\lambda) \delta_{\text{HONO}}(\lambda) d\lambda, \quad (10)$$

In the experiments with LED lamps as light sources, $I(\lambda)_{\text{indoors}}$ can be obtained from the LED emitting spectrum assuming that the light intensity is uniform in the OPC. In the experiments with solar radiation as the indoor light source, $I(\lambda)_{\text{indoors}}$ can be calculated with

$$I(\lambda)_{\text{indoors}} = I(\lambda) \times \text{Transmittance}(\lambda), \quad (11)$$

where $I(\lambda)$ and Transmittance$(\lambda)$ denote the outdoor solar spectrum and transmittance of the dormant window glass at the top of the OPC, respectively. The outdoor solar spectrum was recorded in real time with a CCD spectrometer during the OPC experiments.

The HONO ventilation loss ($d\left[HONO\right]_{\text{vent}}/dt$) can be determined via the ventilation lifetime and the concentration gradient from the OPC to the ambient environment. The HONO concentration in the OPC should be much higher than that in the ambient environment. The ventilation loss can be simplified, as expressed in

$$\frac{d[HONO]_{\text{vent}}}{dt} = [HONO]_{\text{indoors}} \times k_{\text{vent}}, \quad (12)$$

where $k_{\text{vent}}$ denotes the ventilation rate. As stated above, $d[HONO]_{\text{vent}}/dt$ was set to 0.48 × [HONO]$_{\text{indoors}}$ h$^{-1}$ in the OPC experiment.

In our OPC experiment, the variation in HONO did not depend on the temperature (please refer to Section 3.1) in the daytime when HONO accumulation was remarkable, suggesting a slight effect of partitioning and diffusion on the various HONO budget terms [10, 48]. Assuming simultaneous equilibria between HONO and the surface nitrite reservoir, $F_{\text{des}}$ and $F_{\text{ads}}$ could be offset when adopting equations (5) and (6) (i.e., equation (4)) to calculate the raw HONO accumulation rate.

$$\frac{d[HONO]_{\text{imp}}}{dt} \text{can finally be determined by combining all the information and equation (4)-(6). With knowledge of}$$

$$\frac{d[HONO]_{\text{imp}}}{dt}, \text{the HONO production flux in mole m}^{-2} \text{h}^{-1}, F_{\text{HONO}}, \text{in the OPC can be obtained with}$$

$$\frac{d[HONO]_{\text{imp}}}{dt} = F_{\text{HONO}} \times \frac{S_{\text{shining}}}{V}. \quad (13)$$

With knowledge of $F_{\text{HONO}}$, the HONO production rate in mole h$^{-1}$ can be further defined as

$$P_{\text{HONO}} = F_{\text{HONO}} \times S_{\text{Shining}}. \quad (14)$$

Moreover, the photolysis rate constant of surface nitrate can be calculated with

$$j_{\text{surface nitrate}} = \frac{P_{\text{HONO}}}{N_{\text{nitrate}}}, \quad (15)$$

where $N_{\text{nitrate}}$ denotes the abundance of surface nitrate (in mole) under exposure to lighting. Combining equations (2), (3), and (15), the reactive cross section of surface nitrate can finally be constrained (equation (16)) given the dependence of $\sigma_{\text{re}}(\lambda)$ on the surface nitrate density and the $\sigma_{\text{re}}(\lambda)$ profile previously measured [32, 37, 44].

$$j_{\text{surface nitrate}} = \int_{\text{cutoff}}^{605} I(\lambda)_{\text{indoors}} \sigma_{\text{re}}(\lambda) d\lambda. \quad (16)$$

Due to the lack of surface nitrate density ($D_{\text{nitrate}}$) measurements and the nonlinear relationship between $\sigma_{\text{re}}(\lambda)$ and $D_{\text{nitrate}}$ [32, 34, 37, 44], we assumed a certain $D_{\text{nitrate}}$ (or $N_{\text{nitrate}}$) value to obtain $j_{\text{surface nitrate}}$. The range of indoor surface nitrate was reported to be varying from 10$^{-3}$ to 10$^{-5}$ mol m$^{-2}$ [49]. An average $D_{\text{nitrate}}$ of 1.0 × 10$^{-4}$ mol m$^{-2}$ [50, 51] was used in both OPC experiments and later in the ICM simulation (see Section 2.3). The $\sigma_{\text{re}}(\lambda)$ value in the OPC experiment was finally determined by comparing the experimentally determined $j_{\text{surface nitrate}}$ value and our previous laboratory-measured $\sigma_{\text{re}}(\lambda)$ value (Figure S5), the difference of which highlights the different surface nitrate densities between the OPC experiment and our previous studies. Note that the HONO production rate extrapolated to real indoor environments is not affected by the assumed surface nitrate density when the surface nitrate density in the OPC experiment matches that in real indoor environments, whether 10$^{-3}$, 10$^{-4}$, or 10$^{-5}$ mol m$^{-2}$. The redshifted and enhanced absorption of surface nitrate [44] accounted for the observed HONO production with a cutoff of 425 nm, emphasizing this source with photochemical implications under visible irradiation.
corresponding HONO production flux and accumulation rate in the OPC is summarized in Figure 1. In the OPC experiment, we measured the HONO accumulation rate and followed the OPC calculation flow (Figure 1) to validate the reactive cross section, which was measured in our previous laboratory study [44]. Alternatively, we could predict the HONO accumulation rate in the OPC based on previously reported reactive cross section values, following the ICM calculation flow (please refer to Section 2.3). The obtained \( \sigma_r(\lambda) \) values followed the OPC calculation flow could be used to verify whether surface nitrate photolysis could reproduce the HONO accumulation rate according to the ICM calculation flow.

2.3. ICM Construction for a Simulated Room. An ICM was constructed following the calculation structure stated above facilitating either HONO budget analysis of typical indoor environments or data analysis for OPC experiments. The ICM reproduced the measured HONO accumulation rate during the OPC experiment, validating the ICM method for indoor environments.

As described in Section 2.2, \( \gamma_J, S_{\text{shining}}/V, S - S_{\text{shining}}/V, \) and \([NO_2]\) are major variables of \( \text{d}[\text{HONO}]_{\text{NO}_2}/\text{dt} \). Likewise, \( k_{\text{aer}} \) is the determining factor of \( \text{d}[\text{HONO}]_{\text{vent}}/\text{dt}, \) and \( I(\lambda)_{\text{indoor}} \) is important for \( \text{d}[\text{HONO}]_{\text{pl}}/\text{dt} \) and \( \text{d}[\text{HONO}]_{\text{imp}}/\text{dt} \). These factors were reset in the simulated room to evaluate HONO production in typical indoor environments. The dimensions of the simulated room are summarized in Table S2. The simulated room was established with an area of 15 m\(^2\) and a ceiling height of 2.4 m, which yielded an S/V ratio of 1.9 m\(^{-1}\), nearly 6 times lower than that of the OPC. To simplify the sunlight area calculation process of the simulated room, which is a function of the time of day, a dormant window was assumed. Therefore, the sunlight area remained constant at 15 m\(^2\) during the day, which is much larger than the window area of 4 m\(^2\) previously used [14]. The wall surface of the simulated room was assumed to be painted with commercial material and well-aged in the atmosphere, as is commonly encountered in real indoor environments. Filtered solar radiation via a glass window was the only light source in the daytime (06 am–06 pm) for the simulated room, and an LED lamp was the light source during the nighttime (06 pm–06 am). The outdoor solar spectrum refers to our measurements on October 5, 2020, in Beijing (Figure S3). We configured high, medium, and low transmittance values (Figure S2), which varied with the window type, as reported by Blocquet et al. [4]. A commonly used LED lamp (60 W) was the assumed indoor light source. The ventilation rate was set to approximately 0.65 h\(^{-1}\) [52], which yields a ventilation lifetime of approximately 1.54 h, slightly lower than the ventilation lifetime (~2 h) of our OPC. The ventilation lifetime setup corresponds to reality since ventilation lifetimes ranging from 0.29 to 3.45 h in fall and 0.72 to 8.33 h in winter were observed in different indoor environments in a long-term study (a median of 0.87 h in fall and 1.85 h in winter) [53]). A low ventilation rate leads to high indoor HONO accumulation in the ICM but does not change the HONO budget, which is of the highest concern in this study. \([NO_2]\) was set to 50 ppbv under all the conditions.

The major HONO budget terms of the simulated room are summarized in Table 1. The indoor HONO sources included surface nitrate photolysis and photoenhanced heterogeneous reactions of NO\(_2\) on indoor surfaces. The indoor HONO sinks included HONO ventilation and photolysis losses. Other gas-phase reactions, such as OH radical oxidation of HONO as a HONO sink and the recombination reaction between OH radicals and NO as a HONO source, were negligible and were not considered. Direct emission sources of HONO in indoor environments, such as off-gassing from indoor walls and combustion processes such as burning candles, cooking, cigarette smoking, and open fireplaces [13], were also not considered. The major HONO sources and sinks jointly determine the HONO accumulation rate in the simulated room.

Here, the ICM was employed to simulate four scenarios (S1, S2, S3, and S4) to better cover the variations in real indoor environments (Table S3). S1, S2, and S3 are scenarios involving medium-, high-, and low-transmittance glass windows [4], respectively, in a normal room, with a \( \gamma_J \) value of 1 × 10\(^{-8}\), similar to our OPC chamber and previously reported for living rooms and bedrooms [14]. High-transmittance glass windows and a high \( \gamma_J \) value of 5 × 10\(^{-7}\) were set in S4 to establish a kitchen scenario. The corresponding surface nitrate photolysis rates were 2.5 × 10\(^{-7}\) (S1), 1.0 × 10\(^{-7}\) (S2), and 8.4 × 10\(^{-8}\) s\(^{-1}\) (S3) in the daytime and 7.6 × 10\(^{-8}\) s\(^{-1}\) at night. Previous evaluation of surface nitrate photolysis rate in the indoor environment was not directly available. By assuming surface nitrate photolysis as the only indoor HONO source and a nitrate
Table 1: Major HONO budget and typical parameter settings in the indoor photochemical model (ICM). The daytime indoor light intensity in the ICM was determined by the solar radiation and transmittance setup. The nighttime indoor light intensity in the ICM was assumed to be the same as the spectrum of LED lamps and evenly distributed. Emission sources of HONO were not considered in the ICM.

<table>
<thead>
<tr>
<th>Terms</th>
<th>Reaction</th>
<th>Parameter</th>
<th>Model setting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface HNO₃ or NO₂⁺hv (λ ≥ 290 nm)</td>
<td>J_surface_nitrate_indoor (s⁻¹)</td>
<td>Noontime value: 2.5 × 10⁻⁷ (high), 1.0 × 10⁻⁷ (medium), 8.4 × 10⁻⁸ (low)</td>
</tr>
<tr>
<td></td>
<td>(↔) HONO</td>
<td>η₀ and EF</td>
<td>Nighttime value: 7.6 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>γ₀; 1 × 10⁻⁸ (normal room), 5 × 10⁻⁷ (kitchen)</td>
</tr>
<tr>
<td></td>
<td>NO₂⁺surface (λ ≥ 290 nm) ↔ HONO</td>
<td>J_HONO_indoor (s⁻¹)</td>
<td>Noontime value: 2.1 × 10⁻⁴ (high), 2.6 × 10⁻⁷ (medium), 5.4 × 10⁻⁷ (low)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>k_eff (h⁻¹) 0.65</td>
</tr>
</tbody>
</table>

a,b The value is given based on the solar radiation recorded on October 5, 2020, at the PKU site. High, medium, and low denote the noontime J_surface_nitrate_indoor or J_HONO_indoor levels under the high-, medium-, and low-transmittance scenarios, respectively.

The diel variations in HONO_indoor (Figure 3(a)) revealed that the mixing ratios of HONO_indoor in the daytime were much higher (9.5 ± 5.1 ppbv; median: 8.6 ppbv) than those in the nighttime (3.1 ± 0.8 ppbv; median: 2.8 ppbv) with a maximum (16.1 ± 5.4 ppbv) at noon, whereas HONO_outdoor (Figure 3(b)) during the same period exhibited higher values in the nighttime (0.97 ± 0.59 ppbv; median: 0.86 ppbv) than those in the daytime (0.39 ± 0.50 ppbv; median: 0.24 ppbv) with a minimum (0.17 ± 0.12 ppbv) at noon. Moreover, the HONO/NO₂_indoor values in the daytime (0.755 ± 0.433; median: 0.729) were much higher than those in the nighttime (0.138 ± 0.057; median: 0.122), which further highlights greater indoor HONO accumulation in the daytime than in the nighttime. In contrast, slightly higher HONO/NO₂_outdoor values were observed in the nighttime (0.033 ± 0.015; median: 0.030) than in the daytime (0.030 ± 0.014; median: 0.027). To note, it has not been observed indoors the distinct HONO diel variations with a maximum at noon. Previous direct HONO measurements in real indoor environments with UV transmission indicated that HONO diel variations could be perturbed by its fast photolysis or impacted by other factors, such as the temperature and RH [10, 12, 58]. However, our measured HONO_indoor values were comparable

3. Results and Discussion

3.1. Indoor HONO Accumulation in the OPC Experiment. In the OPC experiment (October 4–7, 2020), we observed substantial variations in the HONO mixing ratio in the chamber, HONO_indoor (Figure 2(b)). HONO_indoor varied between 2.2 and 20.3 ppbv (mean = 6.3 ppbv; median = 4.1 ppbv; mode = 5.0 ppbv), whereas the ambient HONO mixing ratio, HONO_outdoor, ranged from 0.07 to 2.4 ppbv (mean = 0.7 ppbv; median = 0.5 ppbv; mode = 0.4 ppbv) during the same period. The HONO_indoor average value was approximately 10 times the HONO_outdoor average value, suggesting the presence of indoor sources, in accordance with previous studies [10, 48]. Moreover, regarding

NO₂⁻ in the chamber, NO₂⁻_indoor varied between 6.1 and 32.5 ppbv and exhibited a similar trend to that of ambient NO₂⁻, i.e., NO₂⁻_outdoor. The HONO/NO₂ ratio was calculated in both the chamber (HONO/NO₂_indoor) and ambient environment (HONO/NO₂_outdoor) (Figure 2(d)). The estimated HONO/NO₂_outdoor levels (0.032 ± 0.015; median: 0.028) were comparable to previously measured outdoor ratios [48] but were much lower than the HONO/NO₂_indoor levels (0.448 ± 0.445; median: 0.206). The average HONO/NO₂_indoor is higher than the HONO/NO₂ ratio of 0.36, 0.17, 0.08, and 0.13 measured in Guangzhou lab room [54], Californian homes [56], residences at Albuquerque [57], and Toronto [10], respectively. High HONO/NO₂_indoor levels are mainly driven by fast HONO accumulation, as indicated in the time series of HONO and NO₂⁻.

The diel variations in HONO_indoor (Figure 3(a)) revealed that the mixing ratios of HONO_indoor in the daytime were much higher (9.5 ± 5.1 ppbv; median: 8.6 ppbv) than those in the nighttime (3.1 ± 0.8 ppbv; median: 2.8 ppbv) with a maximum (16.1 ± 5.4 ppbv) at noon, whereas HONO_outdoor (Figure 3(b)) during the same period exhibited higher values in the nighttime (0.97 ± 0.59 ppbv; median: 0.86 ppbv) than those in the daytime (0.39 ± 0.50 ppbv; median: 0.24 ppbv) with a minimum (0.17 ± 0.12 ppbv) at noon. Moreover, the HONO/NO₂⁻_indoor values in the daytime (0.755 ± 0.433; median: 0.729) were much higher than those in the nighttime (0.138 ± 0.057; median: 0.122), which further highlights greater indoor HONO accumulation in the daytime than in the nighttime. In contrast, slightly higher HONO/NO₂_outdoor values were observed in the nighttime (0.033 ± 0.015; median: 0.030) than in the daytime (0.030 ± 0.014; median: 0.027). To note, it has not been observed indoors the distinct HONO diel variations with a maximum at noon. Previous direct HONO measurements in real indoor environments with UV transmission indicated that HONO diel variations could be perturbed by its fast photolysis or impacted by other factors, such as the temperature and RH [10, 12, 58]. However, our measured HONO_indoor values were comparable.
overall to reported indoor values ranging from 1 to 20 ppbv for different environments or locations regardless of direct emissions stemming from combustion sources [58, 59].

Daytime HONO\_indoor accumulation likely could not be attributed to NO\textsubscript{2} heterogeneous reactions, as HONO\_indoor was largely independent of NO\textsubscript{2}\_indoor (Figure S6). A linear least-squares fit to the data revealed that HONO\_indoor was weakly correlated with \([\text{NO}_2]\), RH, and \([\text{NO}_2] \cdot \text{RH}\) in both the day- and nighttime (\(R^2 < 0.1\), Table 2 and Figure S6). Daytime HONO\_indoor accumulation was largely controlled by solar radiation. As a result, fine correlations between HONO\_indoor and \([\text{NO}_2] \cdot \text{J}_{\text{nitrate}}\) were established. Previous studies suggested that this correlation supports the photoinduced conversion of NO\textsubscript{2} into HONO under illumination of UV and visible light [14–17]. In this work, OPC window-filtered solar radiation with wavelengths shorter than 425 nm and therefore excluded UV-induced conversion. Photoenhanced conversion of NO\textsubscript{2} into HONO under illumination of visible light on humic acid or polyphenolic films [22, 24–26] cannot be fully excluded here, although OPC chamber surface might be very different from humic acid or polyphenolic films. Correlations between HONO\_indoor and \([\text{NO}_2] \cdot \text{RH} \cdot \text{J}_{\text{nitrate}}\) (\(R^2 = 0.12\)) suggested that the photoinduced conversion of NO\textsubscript{2} into HONO could not be established. Particularly, data retrieved from the high- and low-NO\textsubscript{2} parallel experiments conducted during October 27–30, 2020 (Figure S4) in the OPC, also demonstrated that changes in NO\textsubscript{2}\_indoor (\(\Delta\text{NO}_2 = 20\) ppbv) imposed a minor effect on the HONO mixing ratio (\(\Delta\text{HONO} < 1\) ppbv). Daytime HONO\_indoor accumulation (\(\Delta\text{HONO} = 12\) ppbv) was likely too high for any heterogeneous reaction of NO\textsubscript{2}, especially considering minimum NO\textsubscript{2} mixing ratio in the daytime.

The correlations between HONO\_indoor and daytime photolysis frequencies were reminiscent of the photolysis of surface nitrate [30], the indoor HONO source under
examination in this study. Here, $J_{\text{nitrate}}$, the enhanced photolysis rate constant of surface nitrate could be obtained (equation (16)) based on our previous measurements [44], underlining enhancement in the visible region. Even with UV filtering in the OPC, a considerable $J_{\text{nitrate}}$ value could still be obtained. In fact, a correlation between HONO$_{\text{indoor}}$ and $J_{\text{nitrate}}$ ($R^2 = 0.52$) was established. Furthermore, indoor HONO accumulation was accelerated as the air quality continued to worsen over the three OPC days (Figure 2(b)). This trend might be controlled by the increase in surface nitrate, which occurs in dynamic equilibrium with gaseous HNO$_3$.

The nighttime measurements revealed a remarkable stability of HONO. Weaker formation and a near-steady-state...
equilibrium between HONO and surface nitrite were proposed. The fine correlation between the HONO mixing ratio and temperature at night ($R^2 = 0.54$) supported this proposal [10, 12]. The weak correlation ($R^2 = 0.10$) between the HONO mixing ratio and temperature in the daytime did not necessarily preclude repartitioning between HONO and its surface reservoir but highlighted the likely strong perturbation of the indoor HONO budget by the surface photochemistry.

3.2. HONO Budget in the OPC. $d[HONO]_{\text{indoor}}/dt$ indicated a HONO accumulation trend as the sun rose and a HONO declining trend as the decrease of solar radiation from noon in the daytime and a flat trend in the nighttime (Figure 3(d)). Based on equations (4)–(6), the derived total HONO source exhibited a similar diel profile. Here, we focus on the daytime HONO budget and examine this indoor HONO source. Partitioning between HONO and its surface reservoir was omitted in budget analysis due to a lack of direct measurements. As a result, the nighttime HONO budget was not perfectly constrained. However, this omission should slightly affect the daytime indoor HONO budget constraints. Photochemical sources were carefully examined. The HONO sink via its reaction with OH was estimated but should slightly affect the daytime indoor HONO budget (Table S1). The photoenhanced $y$ spanned over two orders of magnitude as well as an EF lower limit of roughly lower than 10 folds. Heterogeneity in the reactivity of varied surfaces justifies the span, while EF was found to be a function of NO2 concentration, surface photosensitization reactivity, wavelength, and intensity of illuminating light etc. (Table S1). Photoenhanced $y$ was ranging from $10^{-6}$ to $10^{-5}$ on humic acid surfaces and was almost doubled in low-NO2 conditions as relative to high-NO2 conditions in flow tube reactor [24–26], while photoenhanced $y$ on the order of $10^{-7}$ on polyphenolic films was also reported in the presence of visible light [22], representing a much lower value as compared to UV illumination [26]. In our OPC experiment, visible light ($\lambda > 425$ nm) and medium range abundance of NO2 can not ensure a high EF. In addition, the chamber wall was painted white (paint brand: Dulux) and allowed deposited aerosol particles to simulate indoor environments such as bedroom and living room. There was no additional coating of photosensitization materials, such as humic acid or polyphenolic. Finally, an estimated EF value of 6 was applied for noontime irradiation conditions according to previous studies [14] and represented an upper limit value of EF for our OPC experiments. The derived missing source of HONO based on the upper limit $y_0$ and EF decreased to zero in the early morning rush hours and the afternoon rush hours (Figures 3(d) and 4(a)), confirming that contribution of NO2 heterogeneous reactions evaluated here represented its upper limit.

Under the above assumptions and the concept of photoenhanced uptake of NO2 by wall surfaces, the HONO source strength resulting from NO2 heterogeneous reactions, $d[HONO]_{\text{NO2}}/dt$, exhibited a distinct diel shape with a noontime maximum, as evaluated by equations (7)–(8). The enhanced daytime $d[HONO]_{\text{NO2}}/dt$ value could mainly be attributed to the uptake enhancement with increasing light intensity [14], while the lower NO2 concentration in the daytime than that in the nighttime partly could offset this enhancement. The daytime average $d[HONO]_{\text{NO2}}/dt$ value of $1.09 \pm 0.42 \text{ppbv h}^{-1}$ accounted for 22.8% of the total source rate. The missing source rate ($= d[HONO]_{\text{indoor}}/dt + d[HONO]_{\text{vent}}/dt - d[HONO]_{\text{NO2}}/dt$) exhibited a nearly identical variation to that in HONO_indoor, accounting for 77.2% of the total source rate in the daytime and 67.2% of the all-day average. The unknown source with photochemical properties was thus examined against surface nitrate photolysis, according to previous reports on indoor HONO sources [30]. One could obtain $d[HONO]_{\text{imp}}/dt$ from surface nitrate photolysis induced by visible light using the ICM calculation flow (Figure 1) given the obtained reactive cross section (please refer to Sections 2.2 and 2.3 and Figure S5). $d[HONO]_{\text{imp}}/dt$ indicated similar diel variations and a noontime maximum as the missing source (Figure 4). A linear least-squares fit to the data revealed that $d[HONO]_{\text{imp}}/dt$ and the missing

### Table S1

<table>
<thead>
<tr>
<th>Sample</th>
<th>EF (ppbv h$^{-1}$)</th>
<th>$\gamma$ (ppbv h$^{-1}$)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic acid</td>
<td>6</td>
<td>~0.5</td>
<td>Low reactivity</td>
</tr>
<tr>
<td>Polyphenolic</td>
<td>6</td>
<td>~0.5</td>
<td>Low reactivity</td>
</tr>
</tbody>
</table>

### References

10, 12, 14, 15, 18, 22, 24–26, urban grime [29], glass windows in bedrooms and living rooms under dark conditions [14], spanned across two orders of magnitude and suggested heterogeneity in the surface reactivity toward NO2.
source rate were suitably correlated \( (R^2 = 0.50, \text{ slope } = 0.72) \). It could be concluded that the photolysis of surface nitrate, an indoor HONO source, mainly accounted for indoor HONO accumulation in the OPC.

3.3. Evaluation of This Indoor HONO Source in Real Indoor Environments. Direct extrapolation of this HONO source to typical residential rooms and workplaces is feasible. First, considering the OPC chamber wall surface, Dulux latex paint is widely used in room decoration. Second, the chamber glass windows can mimic room windows in terms of UV filtering. Finally, the chamber was conditioned before the experiment and ventilated with ambient air during the experiment to mimic real gas–wall interactions in actual indoor environments. The success of our model in reconstructing the HONO budget in the OPC also supports the evaluation of indoor HONO accumulation in real indoor environments.

Daily average HONO accumulation levels of 2.4, 1.6, 1.4, and 29.4 ppbv were reached under the S1, S2, S3, and S4 scenarios, respectively (Figure 5). Except for S4, these HONO values agree with the range in literature reports [55, 58] considering indoor environments free of combustion sources. The two photochemical processes on wall surfaces could therefore account for daytime HONO accumulation in typical living rooms and bedrooms. However, the rapid buildup to elevated HONO levels with maximum steady-state mixing ratios higher than 50 ppbv during cooking in kitchens [48, 60] confirms that secondary HONO formation indoors is generally less important than primary emission in kitchens.

Budget analysis suggests that the two complementary processes, i.e., heterogeneous NO\(_2\) reactions and surface nitrate photolysis, contribute 47.3% and 52.7%, respectively, under S1, 54.1% and 45.9%, respectively, under S2, and 57.6% and 42.4%, respectively, under S3 (Figure 5). Compared to heterogeneous NO\(_2\) reactions, HONO Production resulting from surface nitrate photolysis was even stronger or at least comparable. This could be primarily attributed to the higher daytime photolysis rate constant of surface nitrate. With the noontime photolysis rate constant reaching \( 2.5 \times 10^{-7}, 1.0 \times 10^{-7}, \) and \( 8.4 \times 10^{-8} \) s\(^{-1}\), the corresponding HONO emission rates are \( 4.0 \times 10^{-7}, 1.7 \times 10^{-7}, \) and \( 1.4 \times 10^{-7} \) mole h\(^{-1}\) m\(^{-2}\), respectively, for high- (S1), medium- (S2), and low-transmittance (S3) glass windows [4] (Figure S2), respectively, in a typical living room or bedroom. The noontime indoor HONO Production rate from surface nitrate photolysis are 4.1, 1.8, and 1.4 ppbv h\(^{-1}\) under S1, S2, and S3, respectively. Heterogeneous NO\(_2\) reactions and surface nitrate photolysis contributed 95.3% and 4.7%, respectively, under S4 when the primary emission source of HONO in the kitchen was not considered. The upper limit reaction rate of NO\(_2\) partly accounted for its higher contribution to the HONO source budget under S4. Moreover, surface nitrate photolysis strongly depends on the UV availability, which was negligible under the median- and low-transmittance conditions of S2 and S3 relative to the high-transmittance conditions of S1. As a result, surface nitrate photolysis under S2, S3 represented the lower evaluation limit. Overall, S4 simulated extreme conditions where heterogeneous NO\(_2\) reactions are the most important factor and surface nitrate photolysis is the least important factor. The considerable contribution of surface nitrate photolysis, relative to heterogeneous NO\(_2\) reactions, provided robust validation of this indoor HONO source (surface nitrate photolysis) in various real indoor environments.

Due to the notable dependence of surface nitrate photolysis on the UV availability, the contribution of LED light sources was negligible relative to filtered solar radiation under all transmittance conditions (Figure 5). This result

![Figure 4: Comparison between the measured unknown source rate (Missing source) and the calculated source rate from surface nitrate photolysis \( (d[HONO]_{snp}/dt) \) in the OPC experiments.](image-url)
not only agrees with the results of previous studies [46] but also supports our OPC experiments involving LED light sources without HONO production (not shown). While solar UV light is highly important, solar visible light also contributed 35.1%, 58.9%, and 59.3% to the total daytime sources under scenarios S1, S2, and S3, respectively, due to the much higher photon density of visible light than that of UV light.

Ventilation is a simple and effective way to reduce the levels of indoor pollutants upon outdoor–indoor transport. To assess the model sensitivity and determine the ventilation rate needed to suppress indoor HONO accumulation, we modeled the maximum HONO formation around noon (from 1100 to 1300) as a function of the ventilation rate (Figure 6). The required ventilation rates to reach an outdoor average HONO level of 1.44 ppbv [61] in Beijing were 1.5 and 1.7 h\(^{-1}\) at noon under scenarios S3 and S2, respectively, due to the much higher photon density of visible light than that of UV light.

Ventilation is a simple and effective way to reduce the levels of indoor pollutants upon outdoor–indoor transport. To assess the model sensitivity and determine the ventilation rate needed to suppress indoor HONO accumulation, we modeled the maximum HONO formation around noon (from 1100 to 1300) as a function of the ventilation rate (Figure 6). The required ventilation rates to reach an outdoor average HONO level of 1.44 ppbv [61] in Beijing were 1.5 and 1.7 h\(^{-1}\) at noon under scenarios S3 and S2, respectively, with low and medium transmittance levels in the living room. Under low transmittance, a typical ventilation rate ranging from 0.1–4 h\(^{-1}\) [53] could lead to a noontime HONO accumulation level ranging from 14.3–0.5 ppbv. Under ventilation rate upper limits of 3.46 h\(^{-1}\) in fall and 1.39 h\(^{-1}\) in winter [53], noontime HONO accumulation levels could still reach up to 1.28 and 3.0 ppbv, respectively, posing a potential health threat to residents given the high transmittance in living rooms at noon. Under low-transmittance conditions, median ventilation rates of 1.15 h\(^{-1}\) in fall and 0.54 h\(^{-1}\) in winter [53] could lead to noon-time HONO accumulation levels of 1.8 and 3.8 ppbv, respectively, reflecting effective management of indoor HONO accumulation. Overall, mere ventilation could insufficiently suppress indoor HONO accumulation due to photoenhanced secondary production. A low-transmittance window is highly encouraged for the sake of the health of residents.

3.4. Uncertainties. Even though we could not obtain firm conclusions regarding the exact mechanism of HONO formation, this work revealed that instantaneous heterogeneous NO\(_2\) conversion is not the only HONO source in the OPC experiment. We propose that HONO emission results from surface nitrate photolysis, including both direct nitrate photolysis and surface catalytic reactions. Other light-dependent reactions, such as the photolysis of nitrogen compounds (e.g., humic acid), could contribute to daytime HONO accumulation [39] but were not included in our data analysis scheme for the OPC experiment. The omission of
equilibrium-type processes did not prevent us from successful reproduction of the HONO observation. However, equilibrium-type processes are shown to be an important HONO source or sink in real indoor environments [10, 12]. The omission of equilibrium-type processes therefore may cause the model to slightly underestimate HONO once the release of HONO from inner reservoir becomes predominant under the low HONO mixing ratios in the morning and to slightly overestimate HONO once HONO partitioning into the inner reservoir prevails under the high HONO mixing ratios in the afternoon (Figure 4). Notably, the chemical processes of surface nitrate photolysis were the key model elements, which are essential for the model to reproduce our observation in OPC.

As for the ICM evaluation of indoor HONO sources in real indoor environments, we focus on as well the two major daytime HONO sources responsible for the noontime maximum. However, under different environmental conditions, the major influencing factors could change to gas–surface partitioning affected by the temperature or heterogeneous NO2 reactions affected by RH [58]. An increase in the HONO source derived from surface nitrate photolysis could either lead to direct HONO accumulation or surface storage as nitrite ions, which are subsequently released into the indoor environment. This behavior should be examined in a wide variety of indoor spaces. In addition, the environmental variability of the two major daytime HONO sources shall be highlighted. ICM representation of such environmental variability could be gained given future measurement constraint of these key kinetic parameters, including not only the window transmittance but also surface nitrate content, γ0 and EF for NO2 heterogeneous reactions, and photolysis rate constant for surface nitrate. For example, when surface nitrate content increased to be one order of magnitude larger than that assumed in OPC chamber (i.e., 10^{-3} versus 10^{-4} mol m^{-2}) and γ0 increased to be 1.0 \times 10^{-7}, the derived noontime photolysis rate of surface nitrate is 1.0 \times 10^{-8} s^{-1} for living rooms with medium transmittance. Thereby, the daytime accumulation of HONO is 5.3–10.3 ppbv, with the surface nitrate photolysis and photoenhanced uptake of NO2 accounting for 19% and 81%, respectively. ICM is therefore useful to analyze indoor HONO budget and guide future strategies to mitigate indoor air pollution. Here in the ICM model S1–S4 scenarios considering only the variability in transmittance and γ0, nitrate photolysis was validated a new source of indoor HONO. As a result of more strong dependence of HONO photolysis on UV than surface nitrate photolysis, indoor environments filtering UV are feasible to lead to indoor HONO accumulation from surface nitrate photolysis. The relative importance of the two chemical sources of HONO, i.e., surface nitrate photolysis and heterogeneous reactions of NO2, could also be specifically evaluated by ICM framework, given proper measurement constraint of the model.

4. Conclusions

In this work, we combined chamber experiments and model simulations to investigate the photochemical formation budget of HONO in simulated OPC and typical real indoor environments. Under UV light filtering in the OPC (λ > 425 nm), HONO accumulation substantially increased or decreased with solar irradiation, suggesting that visible light-induced processes could facilitate considerable daytime HONO production with profound implications for HONO budget analysis in indoor environments under a high photon density of visible light. Weak correlations and opposite diel profiles between HONO and NO2 verified that heterogeneous NO2 reactions slightly affected HONO accumulation. By applying the ICM calculation flow to determine the HONO budget in the OPC, visible light-induced photolysis of surface nitrate accounted for 77.2% of the daytime HONO formation in the chamber. Successful OPC reproduction encouraged further application of the ICM in HONO budget evaluation under high-, medium-, and low-transmittance conditions in typical living rooms and kitchens. The strength of surface nitrate photolysis was found to account for more than 60% of the total daytime HONO accumulation in a typical living room. Even under typical kitchen conditions, surface nitrate photolysis remained a considerable HONO source relative to heterogeneous reactions of NO2 or even the total HONO source budget. The indoor HONO source derived from surface nitrate photolysis was thus consistently validated between our OPC and ICM evaluations.

While surface nitrate photolysis strongly depends on the UV availability, visible light also accounts for 35.1–59.3% of the total daytime HONO production resulting from surface nitrate photolysis. Ventilation cannot effectively dilute the indoor HONO source of a photoenhanced nature around noontime. Window glass with a low or no light transmission in the UV range could greatly suppress secondary indoor HONO production and is highly recommended considering the health of residents.
Data Availability
Data are available upon reasonable request to the corresponding author.

Conflicts of Interest
The authors declare no competing financial interests.

Authors’ Contributions
Youfeng Wang conducted the experiments, carried out the data analysis, and wrote the manuscript. Chunxiang Ye designed this study, supervised the analysis, and revised the manuscript. Chong Zhang and Jianshu Wang provided some data. All authors participated in the interpretation of results and helped to improve the manuscript.

Acknowledgments
This work was funded by the National Natural Science Foundation of China (Grant Nos. 42175120 and 91744206) and the China Postdoctoral Science Foundation (Grant No. 2019 M650353).

Supplementary Materials
Figure S1: configuration of the outdoor photochemical chamber (OPC) at the PKU site; the inlet tube was used to pass the low-NO2 air or high-NO2 air into the chamber during Oct. 27–30, 2020. Figure S2: transmittance of the glass filter used for the outdoor photochemical chamber (OPC) and high-, medium-, and low-transmittance setup for the indoor photochemical model (ICM). Figure S3: outdoor solar flux measured in Beijing on 12:30, October 5, 2020, and LED flux for the indoor photochemical model (ICM). Figure S4: time series of HONO and NO2 mixing ratios in “low-NO2” (daytime on Oct. 27 and 28) and “high-NO2 air” (daytime on Oct. 29) OPC experiments. Figure S5: the reactive cross section (σₑ(A)) obtained by comparing the J_surface_nitrate between the OPC experiment and our previous laboratory-measured σₑ(A) [44]. Figure S6: correlation of HONO concentration in the outdoor photochemical chamber (HONO_indoor) with NO2 (NO2_indoor), J_nitrate, RH, and temperature (Temp.) during the night (plot in black circle) and day (plot in red square), respectively. J_nitrate was calculated based on the measured solar flux, glass transmittance, and reactive cross-section of surface nitrate [44] assuming an average surface nitrate density (1 × 10⁻⁴ mole m⁻²) [50, 51]. Figure S7: diel profiles of ambient temperature (Temp.) and relative humidity (RH) and their respective correlation with the unknown source rate of HONO (missing source) during the OPC experiments. Table S1: overview of photoenhanced uptake coefficients (γ) of heterogeneous NO2 reactions to produce HONO on various surfaces. Table S2: summary of the setup of the outdoor photochemical chamber (OPC) and simulated room in our constructed indoor photochemical model (ICM). Table S3: summary for scenarios considered in the outdoor photochemical chamber (OPC) experiment and indoor photochemical model (ICM). (Supplementary Materials)

References


