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Invited feature article

Nitrous acid (HONO): An emerging indoor pollutant



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ABSTRACT

Nitrous acid (HONO) is an emergent household pollutant exhibiting adverse health effects. It can be easily photodissociated by the solar light penetrating through the windows leading to an important production of hydroxyl radical (OH) which in turn controls the oxidative capacity of indoor atmospheres.

Indeed, recent campaign performed in a school classroom in Marseille, France revealed high levels of OH radicals in order of 10^6 cm^{-3} which were directly associated with the photolysis of HONO. Chamber experiments confirmed that photolysis of HONO is the main source of OH radicals indoors. Very recent laboratory measurements have demonstrated that the photo-enhanced reaction of NO_2 on various surfaces commonly found indoors is a powerful source of HONO indicating that indoor surfaces are not only physical but also photochemical substrates that play an active role in the enhancement of the production of HONO indoors. These results provided a significant contribution towards a comprehensive understanding of HONO chemistry indoors, a knowledge that should be implemented in photochemical models in order to properly describe the indoor air chemistry.

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1. Introduction

People in Western societies spend about 90% of their time indoors, predominantly in their own homes. Concerning the indoor environment we are facing a delicate situation because the global requirement of energy saving leads to increased levels of gas-phase pollutants. Indeed, to reduce their energy costs, low-energy buildings use good insulation, energy efficient windows, low levels of air infiltration and heat recovery ventilation to lower the heating and cooling energy. Due to the smaller volumes and low air exchange rates, the residence time of the air pollutants is much longer indoors in comparison to the outdoor atmosphere [1]. Among all the compounds present in indoor air, nitrous acid (HONO) represents an important gas-phase pollutant which could be present at quite high concentrations exhibiting air quality implications.

1.1. Indoor HONO mixing ratios

Nitrous acid was identified and detected for the first time in the indoor atmosphere by James N. Pitts Jr. [2], a prominent scientist in the field of atmospheric chemistry. Since then, only a few studies have attempted to measure indoor HONO mixing ratios. These limited measurements have demonstrated that indoor HONO

mixing ratios are higher than the outdoor mixing ratios. For example, two years of HONO monitoring in urban area of Shanghai, China, revealed outdoor average HONO mixing ratio of 1.08 ± 0.63 ppb during the night, and 0.76 ± 0.44 ppb for daytime [3]. In 2007, during the campaign held in Beijing, China, the daily average HONO mixing ratios were spanning in the range between 0.03 and 2.9 ppb and did not exhibit time variation between the winter and summer periods [4].

The outdoor mean HONO levels during the day in a rural area of southwest Spain were about 0.3 ppb [5].

On the other hand, it was reported that in the indoor environment a conventional gas-fired kitchen range can result in the rapid build-up of elevated HONO levels with maximum steady state mixing ratio of more than 50 ppb of HONO [6]. Vecera and Dasgupta [7] also measured very high indoor HONO mixing ratios in the range between 20 and 90 ppb. HONO levels peaked in the range from 10 to 20 ppb in a study [8] carried out in a dwelling situated at the first floor of a building in the suburbs of Rome, Italy. Another study [9] reported an average value of 5 ppb of HONO in the museum in Rome, Italy. An average HONO mixing ratio of 4.7 ppb was measured in houses at Albuquerque, New Mexico [10]. Simon and Dasgupta [11] measured HONO mixing ratios in the range between 5 and 10 ppb in four different houses. Lee et al. [12] observed an average indoor HONO mixing ratio of 4.6 ppb compared to 0.9 ppb for outdoor HONO during six-day integrated indoor and outdoor measurements in two communities in Southern California. The average mixing ratios of nitrous acid were 6.8 ppb and 3.7 ppb in four homes in residential areas and

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1.4 ppb and 1.2 ppb in two offices in Cairo, Egypt [13]. More recently, Park and Cho [14] performed on-line HONO analysis in a house in Gwangju, Korea. The observed HONO mixing ratios varied between 1.5 and 4.32 ppb depending on the conditions. Finally, Gomez Alvarez et al. [15] measured HONO mixing ratios in the range between 5 and 15 ppb, in a school classroom in Marseille, France over the course of several days during the summer of 2011.

It is also worth mentioning that in the micro indoor environments such as vehicles transiting through polluted urban area in Rome, Italy, HONO mixing ratios of up to 30 ppb (outside mixing ratio of HONO: 1.4 ppb) were detected [16].

All the above measurements indicate that the HONO mixing ratio measured in various indoor environments in EU, US and Asia is variable and strongly dependent on the direct and indirect sources described below.

1.2. Formation of HONO within indoor environments

Indoor HONO can be generated directly during a combustion process [17], that is, in gas stoves and space heaters, burning candles or formed via heterogeneous hydrolysis of NO₂ on various indoor surfaces. Indoors, the surface to volume (S/V) ratios are larger and therefore the potential of HONO production is significantly elevated compared to outdoors. Pioneering scientific investigations by Sakamaki et al. [18] and Pitts et al. [19] focused their work on NO₂ surface chemistry and showed that, indeed, heterogeneous reactions occur on indoor surfaces and can generate indoor HONO concentrations levels that exceed the outdoor HONO concentrations levels.



This observation was recently confirmed in two consecutive studies by Ramazan et al. [20,21]. The heterogeneous reaction that results in indoor HONO production was shown to proceed faster at higher levels of NO₂ and relative humidity. It is now well recognized that indoor levels of NO₂ exceed those found outdoors in polluted urban air. This problem is aggravated in houses with relatively low ventilation rates. The indoor NO₂ mixing ratios are observed to range from 15 to 200 ppb [7,19,22]. The extremely high NO₂ mixing ratios of 1.5 ppm are associated with homes using gas stoves [23]. Given such high indoor NO₂ mixing ratios, it has been postulated that the reason why indoor HONO mixing ratios greatly exceed outdoor levels is that the indoor NO₂ heterogeneous surface wet reactions contribute to the generation of nitrous acid [12].

Although these two processes (direct emission and heterogeneous “wet” reactions) present significant indoor HONO sources, the models accounting only for these two sources systematically underestimate the observed HONO mixing ratios [20,24].

Two recent studies [25,26] have suggested potentially important indoor HONO production pathways, considering that sunlight penetrates indoors (Fig. 1) and initiates photochemistry.

These two studies [25,26] have shown that HONO is produced by light-induced heterogeneous reactions of NO₂ with selected common indoor surfaces such as glass, cleaning detergent, paint and lacquer. The UV fraction of the solar light can enhance the heterogeneous NO₂ to HONO conversion which occurs on various indoor surfaces and increase the HONO yield. In the case of lacquer, one of its constituents that is benzophenone, a known photosensitizer [27–29] was suggested as a reason for the enhanced HONO formation through the heterogeneous reduction of NO₂. The emerged HONO surface flux under light irradiation of the surface covered with lacquer was 2.8×10^{10} molecules cm⁻²s⁻¹ which is of similar magnitude to 2.5×10^{10} molecules cm⁻² s⁻¹ obtained by the heterogeneous reactions of NO₂ with humic acid [30]. These results [25] provide a significant contribution towards the

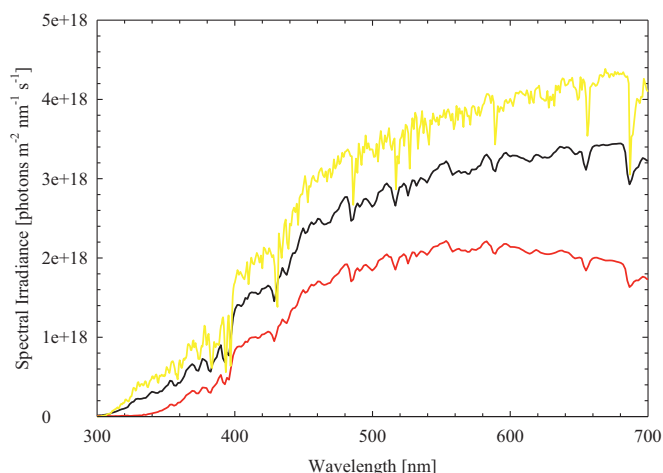


Fig. 1. Solar spectral irradiances were taken on 6th May 2013 at 16:00 in the city centre of Marseille, France (clear sky) on a horizontal surface at 10 cm distance from the window obtained with open windows (outdoors) (black line) and closed windows (indoors) (red line). The spectra were taken in the building oriented North/South at the university campus situated in the city centre of Marseille, France. As a comparison, a standard solar spectral irradiance for solar zenith of 48° and clear sky (yellow line) is shown (American Society for Testing and Materials (ASTM)). This spectrum corresponds to the total irradiance on a surface tilted towards the sun (37°). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

understanding of HONO chemistry indoors, a knowledge that should be implemented in the photochemical models in order to properly describe the HONO values, within indoor environments.

Stemmler et al. [30] estimated that the photochemical HONO formation induced by humic acid contributes by 30% to the OH radical production in the boundary layer of the atmosphere. In a similar fashion, the observed light-induced HONO formation rates on indoor surfaces [25,26] may help to explain the high OH levels (see Section 3) observed indoors during daytime, which cannot be explained by Reaction (R1) [31].

2. Photocatalytic remediation: a possible source of HONO

Common methods of improving indoor air quality include controlling pollution sources, increasing ventilation rates, or using air purifiers. Photocatalytic technology was suggested as an alternative possibility to eliminate indoor air pollutants instead of just diluting or disposing them. It is an excellent example of a remediation technology using sustainable energy as they only require UV–vis light to work. This type of passive technology can greatly reduce other current measures for improving indoor air quality such as mechanical ventilation and air purifiers, which require considerable amounts of electric energy and ultimately do not solve completely the problem.

Photo-catalysts used for air remediation are typically activated by UV light (<390 nm). However, for indoor application more and more photo-catalysts are developed which show promising activity already in the visible range between 400 and 700 nm. Titanium dioxide (TiO₂) is a widely used photo-catalyst [32], which is aimed to eliminate organic and inorganic atmospheric pollutants. TiO₂ nanoparticles are either deposited at the surface of the material (such as glass, pavement . . .) or embedded in paints or concrete.

There are a number of studies that claimed the efficiency of TiO₂ nanoparticles to remove the atmospheric pollutants such as nitrogen oxides (NO_x = NO + NO₂) and volatile organic compounds (VOCs) [33–39]. Although some promising results have been obtained in the past, also the formation of harmful intermediates

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