

Homogeneous and heterogeneous photolysis of nitrate in the atmosphere: state of the science, current research needs, and future prospects

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HIGHLIGHTS

- Recent advances in the photolysis of nitrate/ HNO_3 are reviewed.
- Mechanisms and key factors affecting the photolysis of nitrate/ HNO_3 are summarized.
- Atmospheric implications and future research recommendations are provided.

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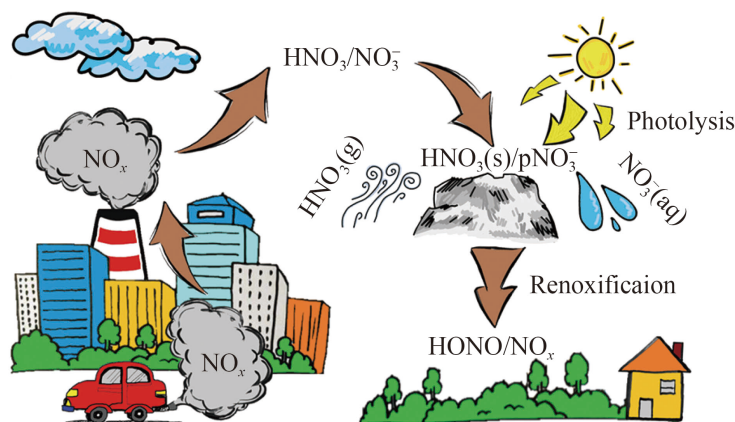
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ABSTRACT

Nitrate is an important component of atmospheric particulate matter and affects air quality, climate, human health, and the ecosystem. Nitrate was previously considered a permanent sink for nitrogen oxides (NO_x). However, this viewpoint has been challenged in recent years because growing research evidence has shown the transformation of nitrate into NO_x (i.e., renoxification). The photolysis of nitrate/ HNO_3 , especially in the particulate phase or adsorbed on particles, can be a significant renoxification process in the atmosphere. The formation and photolysis of nitrate in aerosol not only change the diurnal variation of NO_x , but also provide long-distance transport of NO_x in the form of nitrate, which affects local and regional atmospheric chemistry and air quality. This review summarizes recent advances in the fundamental understanding of the photolysis of nitrate/ HNO_3 under various atmospheric conditions, with a focus on mechanisms and key factors affecting the process. The atmospheric implications are discussed and future research is recommended.

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Special Issue—Visions

1 Introduction

Nitrogen oxides ($\text{NO}_x = \text{NO}_2 + \text{NO}$) are important factors affecting regional air quality, since they are the crucial precursors of ozone in the atmosphere and contribute to

of NO_x in the atmosphere is of great environmental significance, especially the processes of their sources and sinks.

Nitrate is ubiquitous and the main sink of NO_x in the troposphere. HNO_3 /nitrate exists in the gaseous, liquid, and particulate phases. Gaseous HNO_3 can be adsorbed on the surface of particles or react with other species (such as NH_3) to form nitrate and finally enter the particulate phase. Nitrate is one of the main components in both coarse and fine particles, accounting for about 2 %–34 % of atmospheric particulate matter (Sun et al., 2015; Li et al., 2018; van Donkelaar et al., 2019; Shang et al., 2021). The content of nitrate is affected by temperature, relative humidity, and the concentrations of NO_2 , SO_2 , and NH_3 (Sun et al., 2015; Li et al., 2018). Nitrate also exists in the form of the nitrate ion (NO_3^-) in aerosol liquid water under humid conditions because of its high hygroscopicity. Organic nitrates (ONs) in the atmosphere, namely esters containing nitrate groups and their derivatives, also contain $-\text{ONO}_2$ groups bound by covalent bonds (Roberts, 1990; Gu et al., 2017; Yang et al., 2019). ONs are mainly formed through the reaction between VOCs and free radicals with the participation of NO_x . ONs have concentrations of about 0.08–4.0 $\mu\text{g}/\text{m}^3$ and account for 3 %–38 % of organic aerosol in the atmosphere (Rollins et al., 2012; Kiendler-Scharr et al., 2016; Lee et al., 2016). Nevertheless, this review only focuses on inorganic nitrates and does not discuss ONs due to their wide varieties and different properties.

The formation pathways of nitrate in atmospheric particles include gas-phase reactions between NO_2 and OH to form HNO_3 , followed by adsorption on particles or

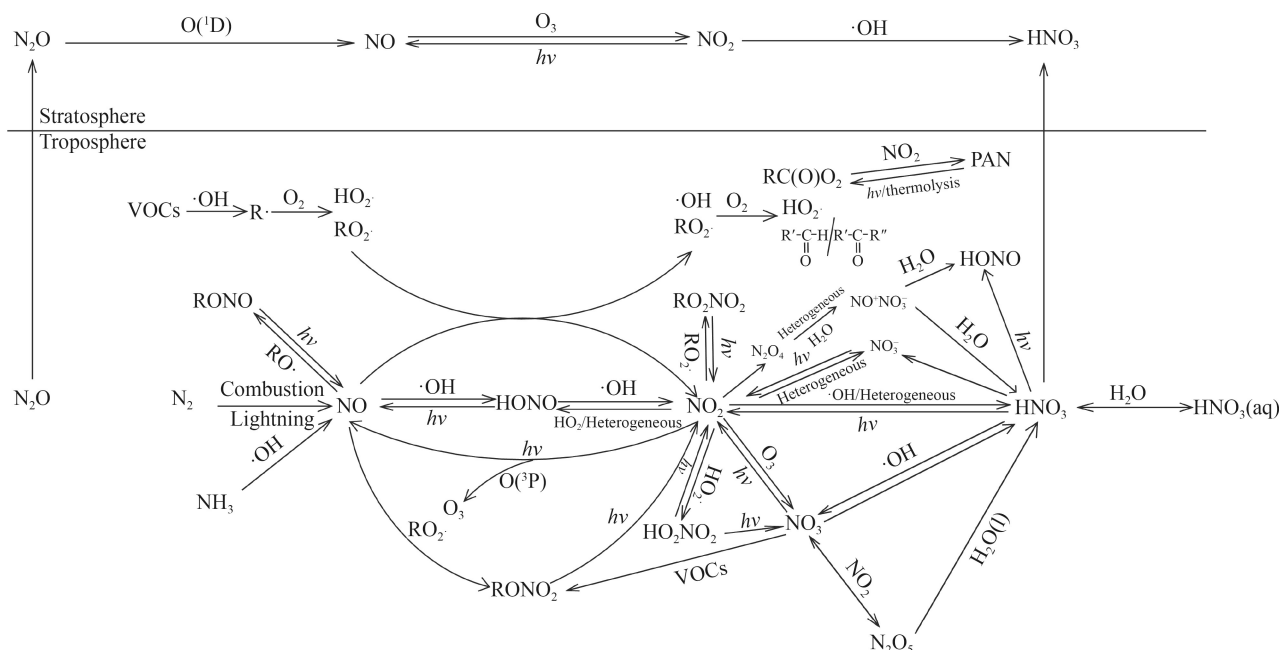


Fig. 1 Atmospheric chemical processes related to NO_x in the atmosphere.

neutralization by NH_3 (Logan et al., 1981; Neuman et al., 2003), hydrolysis of N_2O_5 on wet surfaces (Russell et al., 1986; Ravishankara, 1997; Chang et al., 2011), heterogeneous reactions of NO_2 on aerosol (Goodman et al., 1998; Miller and Grassian, 1998; Finlayson-Pitts, 2003; Usher et al., 2003), and so on. The formation of nitrate is a key process of NO_x removal in the atmosphere because HNO_3 /nitrate has been considered a permanent sink of NO_x (Finlayson-Pitts and Pitts, 2000). However, the discovery of the renoxification process changed this concept of HNO_3 /nitrate being a permanent sink for NO_x . The pathways for HNO_3 /nitrate to be transformed back to reactive gaseous compounds, e.g., NO , NO_2 and HONO , have been called “renoxification” (re- NO_x -ification). For example, NO can react with surface adsorbed HNO_3 to form HONO , which is considered to be a renoxification process of HNO_3 (Fairbrother et al., 1997; Rivera-Figueroa et al., 2003).

In recent years, scientific interest in renoxification has been rekindled by the laboratory observation of rapid photolysis of HNO_3 /nitrate deposited on various mediums in the atmosphere (Honrath et al., 1999; Honrath et al., 2002; Zhou et al., 2003). The photolysis mechanism and rate of HNO_3 /nitrate refer to not only the interaction between HNO_3 /nitrate and light (e.g., characteristic absorption band of nitrate) but also the existence forms of HNO_3 /nitrate, the properties of different substrates and interfaces, relative humidity, and coexisting compounds. The photolysis rate constants of nitrate adsorbed on surfaces vary over 1–4 orders of magnitude, while the reasons for this are not fully understood (Baergen and Donaldson, 2013; Ye et al., 2016; Ye et al., 2017b; Ma et al., 2021). A complete understanding of the photolysis of HNO_3 /nitrate in aerosol particles requires detailed knowledge of the complexity and varying properties of aerosol particles and their effects on kinetics. A recent review by Gen et al. has discussed the factors and mechanisms affecting particulate nitrate photolysis and the reactions initiated by nitrate photolysis in particulate phase (Gen et al., 2022). However, a comprehensive review on the photolysis of nitric acid or nitrate in various phases including gas phase, aqueous phase, and particulate phase, as well as its environmental effects in the atmosphere is still lacking. In this review article, we summarize recent advances in the photolysis of HNO_3 /nitrate, with a focus on the mechanism, kinetics, and key factors affecting the reaction in the gas phase, liquid phase, and particulate phase. The atmospheric implications, especially on atmospheric chemistry and local atmospheric environment, are discussed, and future research is recommended.

2 Experimental requirements for studying nitrate photolysis

As a typical renoxification process, the accurate

measurement of the gaseous products in HNO_3 /nitrate photolysis is a key issue. The optimal experimental approach for this employs a chamber (Shi et al., 2021), close infrared reaction cell (Mochida and Finlayson-Pitts, 2000; Schuttlefield et al., 2008), or flow reactor, such as a cylindrical photochemical flow reactor (Ye et al., 2016; Bao et al., 2018; Xu et al., 2021) or wall-coated flow tube reactors (Yang et al., 2018; Ma et al., 2021). The core components of these systems are the light source, the reactor, and the detection system. The light source is generally a xenon lamp, mercury lamp, or black light lamp that emits visible or ultraviolet light. The reactors are mainly made of light-transmitting inert materials, such as quartz, glass, and polytetrafluoroethylene (Teflon). Analysis of the products of nitrate photolysis includes gas-phase product and ionic composition analysis. Gas-phase products are mainly analyzed by gas analyzers (such as NO_x analyzers and HONO analyzers) and infrared spectroscopy. NO_2^- is the main photolysis product of nitrate ions in the liquid phase and is measured by colorimetry or ion chromatography (Goldstein and Rabani, 2007; Roca et al., 2008; Han et al., 2021).

The experimental results of nitrate photolysis are generally described by the apparent production rate of the product (P_N) and the photolysis rate constant of nitrate ($J_{\text{HNO}_3 \rightarrow \text{N}}$). P_N is calculated by Eq. (1) (Ma et al., 2021):

$$P_N = \frac{F_g \times \int_{t_1}^{t_2} C_N dt}{60 \times 1000 \times (t_2 - t_1) \times R \times T}, \quad (1)$$

where P_N is the observed production rate of the product (10^{-6} mol/s), N represents NO_x or HONO , F_g is the carrier gas flow rate (L/min), R is the gas constant, T is the absolute temperature (K), t_1 and t_2 are the time (min) when the light exposure experiment is started and finished, respectively, C_N is the concentration of the product (ppbv), and 60 and 1000 are unit conversion factors. If the losses in the reactor and the detection process are considered, it is necessary to multiply the results by a certain correction coefficient based on Eq. (1) to correct the results (Ye et al., 2019).

The nitrate photolysis rate constant of a specific product N ($J_{\text{HNO}_3 \rightarrow \text{N}}$) is calculated by Eq. (2) (Ye et al., 2019):

$$J_{\text{HNO}_3 \rightarrow \text{N}} = \frac{P_N \times 10^{-6}}{N_{\text{HNO}_3}}, \quad (2)$$

where $J_{\text{HNO}_3 \rightarrow \text{N}}$ is the observed production rate of the product (s^{-1}) and N_{HNO_3} is the amount of HNO_3 /nitrate (mol).

In general, the product N are mainly NO_2 and HONO , and the overall photolysis rate constant of nitrate can be described as (Eq. (3)):

$$J_{\text{HNO}_3} = J_{\text{HNO}_3 \rightarrow \text{HONO}} + J_{\text{HNO}_3 \rightarrow \text{NO}_x}. \quad (3)$$

Besides, the experimental nitrate photolysis rate constants can be normalized to the photolysis rate

constants under tropical noontime conditions on the ground (solar elevation angle $\theta = 0^\circ$), which can eliminate the effect of different experimental sites on the photolysis rate constant and make different experiment results comparable (Ye et al., 2016).

3 Photolysis of HNO_3 in the gas phase

The formation of HNO_3 in the photochemistry of VOCs- NO_x mixtures means that the chain reaction involving NO_2 molecules terminates and NO_2 exits the NO_x cycle. The concentration of gaseous HNO_3 is about $0.17\text{--}1.1\text{ }\mu\text{g}/\text{m}^3$ with obvious diurnal variation characteristics (Finlayson-Pitts and Pitts, 2000; Chen et al., 2021). HNO_3 is easily adsorbed on the surface or dissolved due to its viscosity and water solubility. Therefore, dry or wet deposition is the main sink of gaseous HNO_3 compared with its reaction with OH radicals (Finlayson-Pitts and Pitts, 2000).

The photolysis products of gaseous HNO_3 include OH radicals, NO_2 , HONO, and $\text{O}(^3\text{P})$ through the following Eqs. (4)–(6) (Kenner et al., 1986; Atkinson et al., 2004; Zhu et al., 2010):



Johnston et al. (1974) speculated that Eq. (4) is the main pathway for the photolysis of gaseous HNO_3 based on the measurement of quantum yield. When the wavelength of light becomes shorter, other channels become more important. Kenner et al. (1986) found that the active intermediate HONO would have a long lifetime and become the main product of gaseous HNO_3 photolysis when in the lowest triplet energy state. Another possible formation mechanism of HONO is the reaction of the excited NO_2 molecule ($[\text{NO}_2]^*$) with H_2O (Eq. (7)) (Li et al., 2008):



However, Zhu et al. (2015) redesigned the photolysis experiment of gaseous HNO_3 under 308 nm light conditions by using cavity ring-down spectroscopy. Their results showed that the NO_2 produced by the photolysis of gaseous HNO_3 is in the standard ground state and has a different spectrum from that of $[\text{NO}_2]^*$. Thus, the excited state of NO_2 produced in the photolysis of gaseous HNO_3 is still unclear. Fig. 2 summarizes the photolysis reactions of gaseous HNO_3 .

The photolysis of gaseous HNO_3 depends on the photochemical absorption cross-section (σ) and the wavelength of the light source. The photochemical absorption cross-section of HNO_3 is in the range of $1.36 \times 10^{-17}\text{--}1.01 \times 10^{-20}$ and $1.01 \times 10^{-20}\text{--}0.42 \times 10^{-23}\text{ cm}^2/$

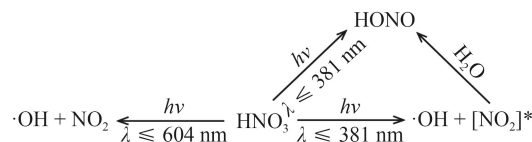


Fig. 2 Photolysis reactions of gaseous HNO_3 .

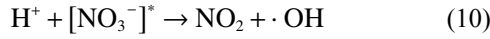
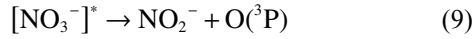
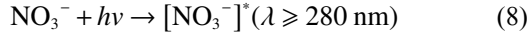
molecule in the wavelength ranges of 190–290 and 290–350 nm, respectively (Finlayson-Pitts and Pitts, 2000). In addition to the light wavelength, temperature and relative humidity can also affect the photolysis of gaseous HNO_3 . Burkholder et al. (Burkholder et al., 1993) showed that the photochemical absorption cross-section and photolysis rate of gaseous HNO_3 increase with the increase of temperature in the range of 240–360 K. An increase in RH can decrease the production of NO_2 and increase the production of NO and HONO in the photolysis of gaseous HNO_3 under 308 nm light conditions (Zhu et al., 2015; Zou et al., 2015). The measured photolysis rate constant of gaseous HNO_3 in the troposphere is about $3 \times 10^{-7}\text{--}7 \times 10^{-7}\text{ s}^{-1}$, which is relatively slow (Ye et al., 2016; Bao et al., 2018; Zheng et al., 2020). Thus, the photolysis of gaseous HNO_3 is not important for the formation of HONO and the renoxification process in the troposphere.

4 Photolysis of $\text{NO}_3^-(\text{aq})$ in liquid phase

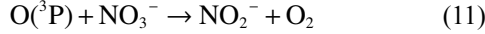
Most nitrates in aerosols have strong hygroscopicity and high solubility, resulting in deliquescence or dissolution into an ionic state under humid conditions. The concentration of $\text{NO}_3^-(\text{aq})$ is affected by aerosol liquid water content, relative humidity, temperature, concentrations of precursors (such as NO_x), and chemical reactions, in which the aerosol liquid water content and humidity are the most influential factors (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2016; Zheng et al., 2020; Wang et al., 2021). Temperature affects the aqueous concentration of $\text{NO}_3^-(\text{aq})$ due to the volatility of nitrate (Seinfeld and Pandis, 2016).

4.1 Photolysis mechanism of $\text{NO}_3^-(\text{aq})$

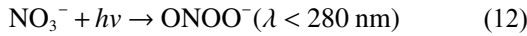
$\text{NO}_3^-(\text{aq})$ is an important photochemically active compound with ultraviolet absorption peaks at 200 nm and 310 nm (Maria et al., 1973). Thus, the photolysis of $\text{NO}_3^-(\text{aq})$ mainly occurs in the ultraviolet band. There are two possible photolysis pathways of $\text{NO}_3^-(\text{aq})$ (Mark et al., 1996; Mack and Bolton, 1999; Dubowski et al., 2001; Roca et al., 2008). One is the transformation of $\text{NO}_3^-(\text{aq})$ into an excited state $[\text{NO}_3^-]^*(310)$ at 310 nm due to the $n \rightarrow \pi^*$ transition (Eq. (8)), and $[\text{NO}_3^-]^*(310)$ further decomposes in two different ways (Eqs. (9) and (10)) (Wagner et al., 1980):



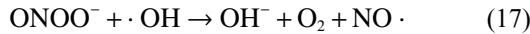
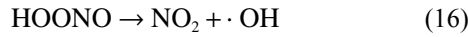
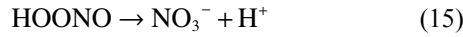
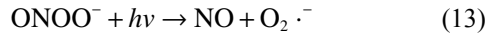
The ground state oxygen atoms will react with $\text{NO}_3^-(\text{aq})$ to form nitrite and molecular oxygen (Eq. (11)) (Wagner et al., 1980):



The other pathway is the transformation of $\text{NO}_3^-(\text{aq})$ into an excited state $[\text{NO}_3^-]^*(200)$ at 200 nm due to the $\pi \rightarrow \pi^*$ transition. Then, $[\text{NO}_3^-]^*(200)$ can either convert into $[\text{NO}_3^-]^*(310)$ or isomerize to peroxyxynitrite (ONOO^-) (Wagner et al., 1980):



The peroxyxynitrite anion can undergo the following reactions (Eqs. (13)–(17)) (Goldstein and Rabani, 2007):

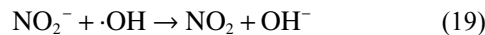


However, there is little research about the second pathway (formation of ONOO^-) at the environmental wavelengths because the reaction needs shorter wavelength than tropospheric actinic radiation and ONOO^- is easily protonated.

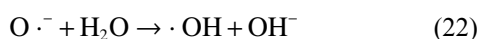
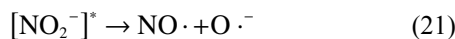
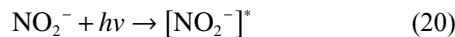
A research focus of the $\text{NO}_3^-(\text{aq})$ photolysis mechanism is the secondary reaction of the photolysis product NO_2^- . These secondary reactions produce different products that affect the apparent quantum yield of $\text{NO}_3^-(\text{aq})$ photolysis. NO_2^- can be protonated under acidic conditions and produce HONO and H_2ONO^+ (Eq. (18)) (Scharko et al., 2014):



NO_2^- can also react with OH radicals to produce NO_2 (Eq. (19)) (Logager and Sehested, 1993):



In addition, NO_2^- also has photochemical activity. The main photolysis products of NO_2^- are OH radicals and NO radicals at wavelengths in the range 200–400 nm (Eqs. (20)–(23)) (Mack and Bolton, 1999):

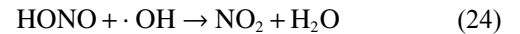


4.2 Main factors affecting the photolysis of $\text{NO}_3^-(\text{aq})$

The products of the photolysis of $\text{NO}_3^-(\text{aq})$ include NO_2^- , OH, HONO and NO_x . NO_2^- and OH radicals are considered the primary products in the photolysis of $\text{NO}_3^-(\text{aq})$, while HONO and NO_x are the subsequent reaction products (Wang et al., 2021). The formation of HONO and NO_x and the quantum yield of NO_2^- and OH radicals in the photolysis of $\text{NO}_3^-(\text{aq})$ depend on a variety of factors such as wavelength, OH scavengers, pH, $\text{NO}_3^-(\text{aq})$ concentration and cations.

The wavelength of the source light affects the quantum yields of the main products directly. In the wavelength range of tropospheric actinic radiation ($\lambda > 290 \text{ nm}$), $\text{NO}_3^-(\text{aq})$ has the highest absorption efficiency for UV light in the vicinity of 310 nm, which can provide higher energy for NO_3^- photolysis and increase the quantum yields of photolysis products (Zafiriou and Bonneau, 1987). Thus, the weak $n \rightarrow \pi^*$ transition absorption band of $\text{NO}_3^-(\text{aq})$ is more important in the troposphere. If the wavelength is less than 200 nm, the strong $\pi \rightarrow \pi^*$ transition may be excited and cause an increase in quantum yields.

OH scavengers affect $\text{NO}_3^-(\text{aq})$ photolysis and its quantum yield by affecting secondary reactions of $\text{NO}_3^-(\text{aq})$ photolysis products. The main product NO_2^- will be consumed by the reaction with OH radicals (Eq. (19)) and OH scavengers can protect NO_2^- , which promote the apparent quantum yield of NO_2^- . NO_2^- can also be protonated under acidic conditions to produce HONO (Eq. (18)) (Scharko et al., 2014) and HONO will react with OH radicals to produce NO_2 (Eq. (24)) (Finlayson-Pitts and Pitts, 2000):



According to Eq. (19), OH scavengers can also enhance the formation of HONO but inhibit the formation of NO_x . Another possible reason for the effect of OH scavengers is the formation of superoxide ($\text{O}_2^-(\text{aq})$). $\text{O}_2^-(\text{aq})$ can react with $\text{NO}_x(\text{aq})$ and produce OONO_2^- and OONO^- . OONO_2^- and OONO^- can be converted to NO_2^- and enhance the apparent quantum yield of NO_2^- and the subsequent formation of HONO.

In addition to impacting the secondary reaction of NO_2^- and the formation of HONO and NO_x , OH scavengers can also enhance the photolysis of $\text{NO}_3^-(\text{aq})$. Han and Mohseni (2020) investigated the effect of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC, such as carbonate) in the liquid phase on the photolysis of $\text{NO}_3^-(\text{aq})$. Their results showed that DOC and DIC in the liquid phase can play roles as OH scavengers and enhance the photolysis of $\text{NO}_3^-(\text{aq})$ through pushing the photolysis equilibrium of $\text{NO}_3^-(\text{aq})$ to the right (Eqs. (8)–(10)). However, the effect of DIC on the photolysis of NO_3^- was not obvious at the low concentration. In conclusion, the main effect of OH

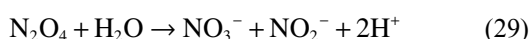
radical scavengers is to consume OH radicals in the liquid phase and affect their reaction with $\text{NO}_3^-(\text{aq})$, $\text{NO}_2^-(\text{aq})$, $\text{HONO}(\text{aq})$, and $\text{OONO}^-(\text{aq})$, which further affect the formation of HONO and NO_x . The scavenging efficiency and rate of OH radical scavengers depend on their reactivity and solubility.

The pH affects the quantum yields of photolysis products by changing the reaction mechanism. Zellner et al. (1990) measured the absolute quantum yields of OH radicals (Φ_{OH}) at 308 and 351 nm in the pH range 4–11, in which thiocyanate ion (SCN^-) was used as an OH scavenger. Their results showed that Φ_{OH} was essentially independent of pH in the range 4–9 and increased with pH in the range of 9–11. Mark et al. (1996) conducted nitrate photolysis experiments in the pH range of 4–13 without OH radical scavengers. Their results showed that the quantum yields of NO_2^- ($\Phi_{\text{NO}_2^-}$) increased with the increase of pH and had a sigmoidal pH dependence. A possible reason is that NO_2^- will be protonated to form HONO which escapes into the gas phase and reduces the apparent $\Phi_{\text{NO}_2^-}$. Another possible reason is that OH radicals will react with peroxyxynitrite anion due to the absence of OH radical scavengers (Eqs. (25) and (26)), which compete with the protonation isomerization of peroxyxynitrite (Eq. (15)):



This competitive process will decrease at high pH, which increases the concentration of nitrate ions, as well as the quantum yields. The pH can also affect the effect of OH scavengers. Scharko et al. (2014) found that the pH dependence of HONO and NO_2 concentrations are more significant in the presence of OH scavengers (such as organic matters, HCO_3^- , and CO_3^{2-}). Benedict et al. (2017) found that the effect of OH scavengers is less effective at low pH.

The $\text{NO}_3^-(\text{aq})$ concentration can affect the initial formation rate and the steady-state concentration of products. Han and Mohseni (2020) found that the initial production rate of NO_2^- first increases and then remains stable with increasing $\text{NO}_3^-(\text{aq})$ concentration. Their explanation is that high-concentration nitrate inhibits the production of OH by water photolysis, thus affecting the formation of nitrite. Another possible reason is the self-inhibition of nitrite, in which nitrite and its radicals (Eqs. (19)–(21)) participate in a complex set of reaction chains to reform nitrate (Eqs. (27)–(30)) (Benedict et al., 2017; Han and Mohseni, 2020):



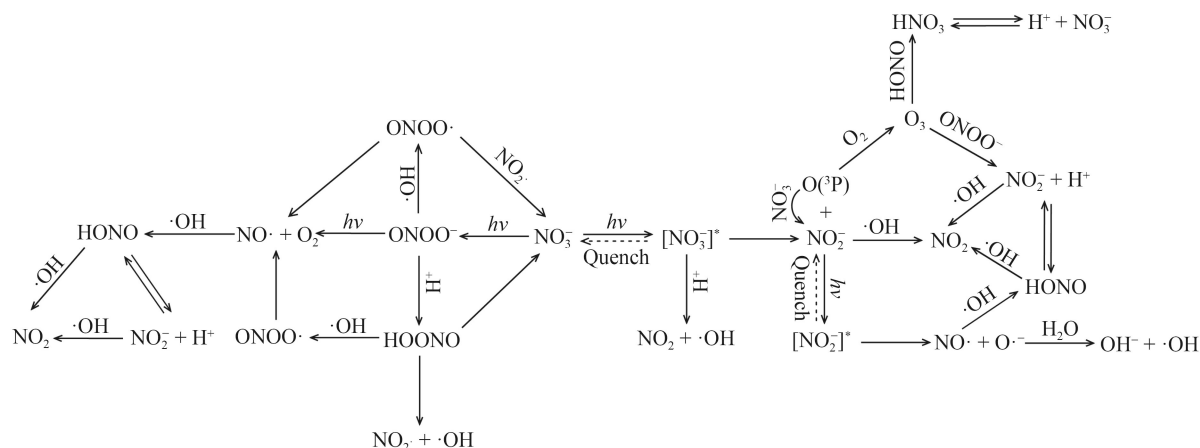
Zepp et al. (1987) also proposed that the quenching effect of nitrate and nitrite is the reason for the deviation from linearity for the relationship between the nitrate photolysis product concentration and $\text{NO}_3^-(\text{aq})$ concentration. However, Brezonik and Fulkerson-Brekken (1998) observed the opposite experimental phenomenon over a wide range of $\text{NO}_3^-(\text{aq})$ concentrations. The possible reason for the discrepancy is differences in the intensity of the light sources.

The effect of cations on nitrate photolysis is not fully understood. Laboratory studies and molecular dynamics simulation suggest that cations do not affect the formation of products in bulk solution, but affect the $\text{NO}_3^-(\text{aq})$ concentration in the air-water interfacial region and thus directly affect the effective quantum yield of $\text{NO}_3^-(\text{aq})$ photolysis (Richards-Henderson et al., 2015; Benedict et al., 2017). Alif and Boule (1991) measured the quantum yield of KNO_3 photolysis ($\Phi_{\text{NO}_2^-}$) to be 6.5×10^{-3} and Roca et al. (2008) reported values for $\Phi_{\text{NO}_2^-}$ from $\text{Ca}(\text{NO}_3)_2$ are 0.23×10^{-3} – 7.8×10^{-3} . Benedict et al. (2017) measured the quantum yields of nitrates with five different cations (K^+ , Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+}), and the results were all close to 1.1×10^{-3} , which suggests that the partner cation of nitrate has no effect on $\Phi_{\text{NO}_2^-}$ in solution. In contrast, their results of $\Phi_{\text{NO}_2^-}$ were twice as high for KNO_3 and much smaller for $\text{Ca}(\text{NO}_3)_2$. However, Richards-Henderson et al. (2015) found the rates of NO_2 for KNO_3 , $\text{Mg}(\text{NO}_3)_2$, and NaNO_3 are 2–3 times higher than $\text{Ca}(\text{NO}_3)_2$ in thin aqueous films, which suggests that cations affect the nitrate photolysis.

The reported quantum yields, photolysis rate constants, and photolysis products of $\text{NO}_3^-(\text{aq})$ in referenced studies are summarized in Table 1, and the photolysis reactions of $\text{NO}_3^-(\text{aq})$ are summarized in Fig. 3. As shown in Table 1, $\Phi_{\text{NO}_2^-}$ is typically an order of magnitude lower than Φ_{OH} and the two quantum yields ($\Phi_{\text{NO}_2^-}$ and Φ_{OH}) correspond to Eqs. (9) and (10), respectively. Due to this difference, previous model studies tended to ignore NO_2^- and subsequent HONO formation, and only focused on NO_2 (Herrmann et al., 1999; Leriche et al., 2000; Frey et al., 2015). However, Benedict et al. have found that the values of $\Phi_{\text{NO}_2^-}$ and Φ_{OH} are comparable in magnitude, which suggests that formation of NO_2^- and HONO from $\text{NO}_3^-(\text{aq})$ photolysis is comparable to NO_2 formation (Benedict et al., 2017). Even so, the absolute values of photolysis rate constants and quantum yield in the photolysis of $\text{NO}_3^-(\text{aq})$ are relatively low, which could be due to the quenching effect of the surrounding solvent, other solutes and nitrate itself causing the photo-excited $\text{NO}_3^-(\text{aq})$ to return to the ground state. Although nitrate photolysis may promote the degradation of soluble organic matter in solution, the photolysis of $\text{NO}_3^-(\text{aq})$ may not be important to the renoxification process in the troposphere. Nevertheless, the enhancement effect of OH scavengers in the aerosol liquid phase and special liquid film environment may increase the importance of

Table 1 Quantum yields, photolysis rate constants, and main photolysis products of nitrate ions in the liquid phase

Conditions	Quantum yields/ Photolysis rate constants	Photolysis products	References
Room temperature pH $\approx$ 6 phosphate buffer $\lambda > 295$ nm organic acid	$3.40\text{--}6.24 \times 10^{-6} \text{ s}^{-1}$	HONO, NO ₂	Wang et al., 2021
295 K pH = 4–9 $\lambda = 290\text{--}420$ nm	$8.5 \times 10^{-7} \text{ s}^{-1}$	HONO, NO ₂ , NO ₂ [−] , OH	Scharko et al., 2014
248–268 K $\lambda = 295$ nm	ΦNO_2^- $1.3\text{--}4.8 \times 10^{-3}$	NO ₂ [−] , OH, NO ₂	Dubowski et al., 2001
278–358 K pH = 8 $\lambda = 351$ nm	ΦOH $2.7\text{--}15.3 \times 10^{-2}$	NO ₂ [−] , OH	Zellner et al., 1990
296–322 K pH = 6.7–8 $\lambda = 298\text{--}371$ nm	ΦOH $1.3\text{--}8.5 \times 10^{-2}$	NO ₂ [−] , OH	Zafiriou and Bonneau, 1987
pH = 4 $\lambda = 310$ nm	ΦNO_2^- $1.4\text{--}4.2 \times 10^{-3}$	NO ₂ [−] , OH	Roca et al., 2008
Room temperature $\lambda = 254$ nm	ΦOH 9.0×10^{-2} ΦNO_2^- 6.0×10^{-3}	NO ₂ [−] , OH	Mark et al., 1996
Room temperature pH = 4–11 $\lambda = 305$ nm	ΦOH $0.87\text{--}1.3 \times 10^{-2}$ ΦNO_2^- $5.5\text{--}8.8 \times 10^{-3}$	NO ₂ [−] , OH	Warneck and Wurzinger, 1988
298 K pH = 3–9 $\lambda = 313$ nm	ΦNO_2^- 1.1×10^{-2}	NO ₂ [−] , OH	Benedict et al., 2017

**Fig. 3** Photolysis reactions of NO₃[−](aq).

NO₃[−](aq) photolysis, and further research is needed to assess the extent of the enhancement and the contribution to the renoxification process.

5 Photolysis of nitrate in the particulate phase

The main existence form of particulate nitrate (pNO₃[−]/HNO₃(s)) depends on the particle size. Particulate nitrate refers to nitrates adsorbed on various surfaces or in deliquescent aerosol particles in this review. In fine

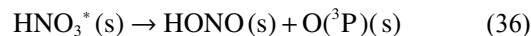
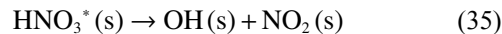
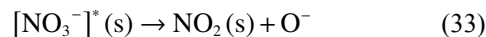
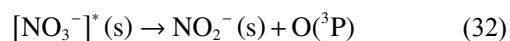
particulate matter, ammonium nitrate (NH₄NO₃) produced by the reaction between nitric acid and NH₃ is the main existence form of pNO₃[−]/HNO₃(s) (Zhuang et al., 1999; Lee et al., 2008; Seinfeld and Pandis, 2016). In contrast, pNO₃[−]/HNO₃(s) exists in the form of metal complexes such as NaNO₃, KNO₃, and Ca(NO₃)₂ rather than NH₄NO₃ in coarse particulate matter, which is mainly due to the reaction of nitric acid or NO₂ with sea salt or mineral dust (Zhuang et al., 1999; Yao et al., 2003; Lee et al., 2008). Since nitrate mainly exists as pNO₃[−]/HNO₃(s) in the atmosphere, the photolysis of pNO₃[−]/HNO₃(s) has received much attention.

5.1 Photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$

Particulate nitrate exists not only in aerosols, but also on various surfaces such as the ground, building surfaces, and plant surfaces. Therefore, the photolysis of adsorbed $\text{HNO}_3(\text{s})$ or mixed $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ on various natural and artificial surfaces, including on model particles (Gankanda and Grassian, 2014; Dyson et al., 2021; Ma et al., 2021), natural atmospheric particulate matters (Ye et al., 2017b; Bao et al., 2018), urban grime (Baergen and Donaldson, 2013; Baergen and Donaldson, 2016), building materials or roads (Ye et al., 2016), plant leaves (Ye et al., 2016), indoor surfaces (Schwartz-Narbonne et al., 2019; Pandit et al., 2021), and ice and snow (Morenz et al., 2016; McFall et al., 2018) has been widely investigated. The wavelength band for $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ photolysis is 290–420 nm, mainly the UV light in the troposphere, and the photolysis rate constant of adsorbed $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ is 1–4 orders of magnitude higher than that of gaseous HNO_3 or NO_3^- in the liquid phase (Ye et al., 2016; Ye et al., 2017b; Yang et al., 2018; Dyson et al., 2021; Ma et al., 2021). It was found that the absorption cross-section of $\text{HNO}_3(\text{s})$ at the wavelengths of 308 nm and 335–365 nm significantly increased compared to gas-phase HNO_3 based on Brewster's angle cavity ring-down spectroscopy measurements (Zhu et al., 2010; Du and Zhu, 2011). The interaction with the substrate is a key reason for the increase in absorption cross-section and the rapid photolysis of adsorbed $\text{pNO}_3^-/\text{HNO}_3(\text{s})$. Ye et al. (2016) suggest that the interactions between $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ and the surface reaction sites or other molecules can distort the molecular structure of nitrate. The distortion can cause enhancement of the photochemical absorption cross-section or the red-shifting of light absorption. In addition, smaller aerosol particles have optical resonance and increase the optical path length and the intensity of internal light through refraction, which may enhance the photolysis of nitrate.

5.2 Photolysis mechanisms of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$

The photolysis pathways of adsorbed $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ include direct and indirect photolysis mechanisms. In the direct photolysis process, $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ absorbs UV light and causes the cleavage of the N-O bonds while the indirect process depends on the photosensitizers (Bao et al., 2020). The direct photolysis mechanism is similar to the photolysis of gaseous HNO_3 , and includes the excitation of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ and the subsequent decomposition (Eqs. (31)–(36)) (Yang et al., 2018; Ye et al., 2019):



where “s” represents surface adsorption. The direct photolysis mechanism plays a dominant role in the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ without coexisting components.

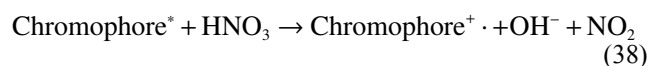
The indirect photolysis mechanism requires the participation of photosensitizers. Photosensitizers are defined as a class of molecules that only absorb photons and transfer energy to other molecules to promote photochemical reactions, but do not participate in the reactions themselves. The primary photosensitizers in the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ are chromophoric organic compounds such as carboxylic acids, aldehydes, benzene, phenols, polycyclic aromatic hydrocarbons (PAHs), and humic-like substances (HULIS). If chromophoric organic compounds exist in the photolysis system, the indirect photolysis process may be dominant.

The photosensitizer is first excited by photons in indirect photolysis (Eq. (37)):

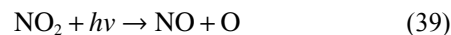


The renoxification process can proceed by the following two pathways after the photosensitizer is excited (Bao et al., 2020):

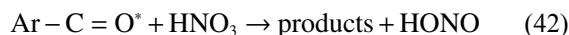
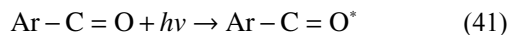
1) The excited photosensitizer transfers electrons to $\text{HNO}_3(\text{s})$, and $\text{HNO}_3(\text{s})$ converts to the anion radical ($\text{HNO}_3^{\cdot-}$). $\text{HNO}_3^{\cdot-}$ further converts to NO_2 (Eq. (38)):



The photolysis of NO_2 can further produce NO or HONO (Eqs. (39) and (40)):



2) Reactive oxygen species (ROS, such as superoxide, oxygenated organic radicals, and hydrated electrons) produced by excited photosensitizers can initiate the renoxification process (Eqs. (41) and (42)) (Han et al., 2016):

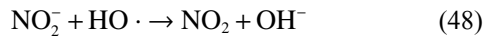
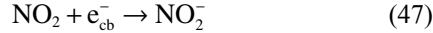
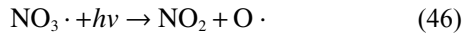
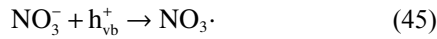
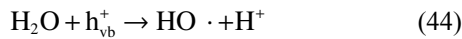
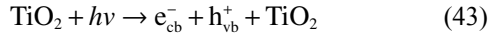


5.3 Main factors affecting the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$

A variety of factors such as the substrate, $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ loading, RH, pH, light source, and coexisting components can affect the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$.

Substrates. The interaction between $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ and various substrates is the most important factor affecting nitrate photolysis. The effects of substrates on

nitrate photolysis are often described as matrix effects. Different from coexisting components, substrate refers to the surface to which $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ is adsorbed. Matrix effects depend on the physicochemical properties of the substrates and the interaction of the substrates with nitrate. Absorbance is the most important physicochemical property, and if the substrate contains photocatalytic components such as TiO_2 , it will promote nitrate photolysis. Xu et al. (2021) studied the matrix effect of TiO_2 on nitrate photolysis. Their experiments find that TiO_2 has a great influence on the flux density of nitrate photolysis products, which is related to the crystal structure and mass ratio of TiO_2 . It was also found that the photolysis of nitrate on the surface of TiO_2 is stronger than that on the surface of Al_2O_3 , SiO_2 or NaY zeolite (Gankanda and Grassian, 2014; Ma et al., 2021). The enhancement of nitrate photolysis by TiO_2 can be explained by the following reactions (Eqs. (43)–(48)) (Xu et al., 2021):



These results are not surprising since TiO_2 is a good photocatalyst material. However, other substances also have enhancement effects on the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$, and the main reason is the interaction of the substrates with nitrate. Ye et al. (2019) studied the matrix effects of various model substrates and proposed that the interaction of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ with the substrate may distort the molecular structure of nitrate, cause the red-shift of the absorption spectrum into the actinic region, and enhance the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$. Recently, it was found that photolysis of nitrate can occur in indoor environments, which could also be possibly attributed to this red-shift effect (Schwartz-Narbonne et al., 2019; Pandit et al., 2021).

Ice and snow are special substrates that exist widely in the world, and the photolysis of nitrate on ice and snow has been widely studied. For enhancement of nitrate photolysis on ice and snow and other comprehensive review, we refer readers to recent review article (Błaszczak-Boxe and Saiz-Lopez, 2018).

Concentration. $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ loading can affect the photoproduction rate or the photolysis rate. Ye et al. (2016) showed that the photolysis rate constant of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ decreases with the increase in the adsorbed HNO_3 /nitrate surface concentration (D_{HNO_3}). A logarithmic relationship between the photolysis rate

constant and D_{HNO_3} was determined according to Eqs. (49)–(51), indicating that a heterogeneous catalysis reaction was involved. High D_{HNO_3} means that the contact between adsorbed HNO_3 /nitrate and the catalytic substrate is reduced, resulting in a decrease in the photolysis rate (Ye et al., 2016).

$$J = \frac{a}{1 + bD_{\text{HNO}_3}} + c, \quad (49)$$

$$P = \int_0^{D_{\text{HNO}_3}} j(D_{\text{HNO}_3}) dD_{\text{HNO}_3} = \frac{a}{b} \ln(1 + bD_{\text{HNO}_3}) + cD_{\text{HNO}_3}, \quad (50)$$

$$J = \frac{P}{D_{\text{HNO}_3}} = \frac{a}{bD_{\text{HNO}_3}} \ln(1 + bD_{\text{HNO}_3}) + c, \quad (51)$$

where j is the photolysis rate constant of each HNO_3 /nitrate molecule, P is the photolysis rate of HNO_3 /nitrate on a unit surface area, J is the average photolysis rate constant of all HNO_3 /nitrate molecules on the surface, and a , b , and c are fitting constants related to the surface adsorption properties. Subsequent experiments on ground aerosol samples collected in Albany (USA) and Delmar (USA) and airborne aerosol samples collected in the Southeast USA also confirmed this conclusion (Ye et al., 2017b). However, Shi et al. (2021) conducted photolysis experiments on suspended submicron particulate nitrate in an environmental chamber, and did not observe any strong dependence for the renoxification rate constant on nitrate mass concentration. This suggests that the mechanism of the effect of nitrate concentration on photolysis is different between adsorption on surfaces and suspended particles, which may be related to the mixing state.

H_2O . H_2O exhibits a positive effect on the photolysis rate constants and the ratio of HONO/NO_x at low RH and the opposite at high RH; however, the RH turning point varies in different studies, from 45 % to 90 % (Bao et al., 2018; Yang et al., 2018; Ye et al., 2019; Ma et al., 2021; Xu et al., 2021).

At low RH, H_2O can participate in the photolysis of nitrate, form a cluster or produce OH radicals with the photosensitizer, thereby promoting the photolysis of nitrate. Ye et al. (2019) proposed that adsorbed HNO_3 and water molecules may form cluster compounds at the surface and increase the photolysis rate constant of nitrate. Bao et al. (2018) evaluated the role of the water in HONO production in the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ on real $\text{PM}_{2.5}$ particles collected in Beijing (China), in which the amounts of both HONO and NO_2 formed are almost below the detection limit at $\text{RH} = 0\%$ but significantly increase under high RH conditions. They proposed that water molecules could directly participate in the photolysis of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ in the form of $\text{H}_2\text{O}/\text{HNO}_3$ clusters (Eq. (52)):



H_2O hinders the photolysis of $\text{HNO}_3(\text{s})$ at high RH. Ye

et al. (2019) showed that water molecules adsorbed on the surface under high RH conditions compete for the active catalytic sites and form water molecular cages, and thus reduce the photolysis rate constant of nitrate. On the other hand, nitrates easily deliquesce under high RH conditions, which is mentioned in Section 4 (Photolysis of NO_3^- (aq) in liquid phase). Ma et al. (2021) propose that nitrate deliquescence will also inhibit the photolysis reaction under high RH conditions and that the influence depends on the hygroscopicity of the particles. Differences in the hygroscopicity of nitrate may be a possible explanation for the observed differences in RH turning points.

In addition, several studies have shown that water molecules will react with photogenerated NO_2 (s) to produce HONO(s) on the surface (Eq. (53)) (Zhou et al., 2003; Yang et al., 2018; Ye et al., 2019):



This reaction does not affect the photolysis of nitrate in theory, but does affect the product distribution of NO_2 and HONO. However, researchers sometimes describe nitrate photolysis in terms of the formation rate of product, and the change in the HONO/ NO_2 ratio can affect the apparent formation rate, which affects the photolysis of nitrate based on the experimental results.

H^+ . H^+ can participate in the photolysis of nitrate directly and affect the release of photolysis products. Bao et al. (2018) found that the production rate of HONO gradually decreased to zero with the irradiation time, and the introduction of HCl flux can restore HONO production under light conditions in the photochemical aging of $\text{PM}_{2.5}$, which is due to the formation of photoactive adsorbed HNO_3 formed from the reaction between H^+ and NO_3^- in $\text{PM}_{2.5}$. Their subsequent experiments also showed that HNO_3 (s) rather than NO_3^- (s) is the main photoactive substance for the photolysis of nitrate to produce HONO, which indicated that H^+ participates in the photolysis process and affects the production of HONO (Bao et al., 2020).

Light. The effect of the light source on nitrate photolysis depends on the wavelength and light intensity. In general, the photolysis rate is proportional to the light intensity and inversely proportional to the wavelength (Gankanda and Grassian, 2014; Bao et al., 2018; Yang et al., 2018; Xu et al., 2021). Compared with visible light, UV light is the main cause of nitrate photolysis. For example, Bao et al. (2018) found that the yield of HONO in the photolysis of real $\text{PM}_{2.5}$ under visible light irradiation ($\lambda > 400$ nm) is 63.1 % lower than that of the full-spectrum irradiated samples at the same light intensity.

In addition to the energy effect brought by the short wavelength, the characteristic absorption band of nitrate could be another important factor. The well-known UV/Vis spectra of NO_3^- (aq) are two absorption peaks at 200 nm and 310 nm as mentioned above. Gankanda and

Grassian found that the nitrate adsorbed on the surface of Al_2O_3 and TiO_2 can photolyze to produce NO_2 at a wavelength of 350 nm (higher than the cut-off wavelength of nitrate absorption), which suggests the red-shift in the absorption spectrum (Gankanda and Grassian, 2014). Therefore, the photolysis enhancement of $\text{pNO}_3^-/\text{HNO}_3$ (s) was attributed to a red-shift in the absorption spectrum (Gankanda and Grassian, 2014; Ye et al., 2019). However, the measurement of the absorption spectrum of $\text{pNO}_3^-/\text{HNO}_3$ (s) is limited.

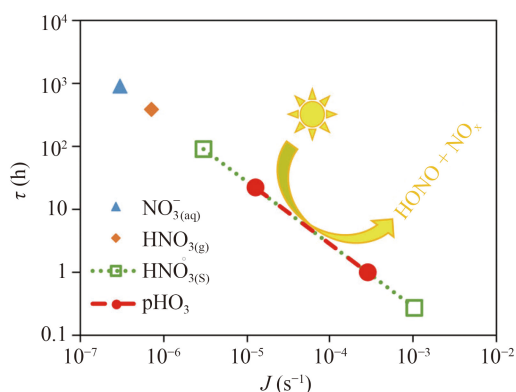
Coexisting components. The effects of coexisting components on nitrate photolysis include both promotion and inhibition. Many coexisting components such as organic compounds, sulfate, and halide ions can enhance the photolysis of nitrate. Coexisting components can affect the acidity of particles and provide H^+ . For example, coexisting sulfate was found to conserve the necessary acidic protons for nitrate photolysis because of the nonvolatility of its conjugated acid (Bao et al., 2020). Coexisting reducing species can also change the distribution of reaction products. Ye et al. (2019) have suggested that coexisting citric acid can reduce photolysis-produced NO_2 to NO . Besides, coexisting components can change the chemical environment and chemical equilibrium. Recent studies have found that SO_2 will enhance the photolysis of nitrate on TiO_2 by altering the equilibrium between the formation and photolysis of nitrate (Ma et al., 2021; Shang et al., 2022). In addition, high-viscosity organics was also proposed to hinder particulate nitrate photolysis (Liang et al., 2021). Other coexisting species such as organics, cations, and halide ions can also affect nitrate photolysis. Their mechanisms include photosensitization, H-donation, and promoting the surface propensity of nitrate anions. For more detailed mechanisms of these factors, we refer readers to the recent review (Gen et al., 2022).

In addition, physical (such as particle size and morphology) and optical properties of aerosols affect the photolysis of pNO_3^- (s) by affecting the distribution of aerosol particles and the intensity of absorbed light. However, there is little research on these factors (Ye et al., 2017b; Liang et al., 2021). Gen et al. (2022) suggested that the aerosol viscosity and Mie resonance may enhance particulate nitrate photolysis through affecting the morphology and optical properties. Other factors such as incomplete solvent cage, ice and snow, temperature, pH and RH can also refer to the review mentioned above (Gen et al., 2022).

Table 2 summarizes the photolysis rate constants of $\text{pNO}_3^-/\text{HNO}_3$ (s) on various surfaces. The photolysis rate constants of $\text{pNO}_3^-/\text{HNO}_3$ (s) vary in the range $1.2 \times 10^{-3} \text{ s}^{-1}$ – $6.0 \times 10^{-6} \text{ s}^{-1}$ due to differences in experimental conditions (surface materials and nitrate samples) (Baergen and Donaldson, 2013; Ye et al., 2016; Ye et al., 2017b, 2019; Ma et al., 2021). Figure 4 illustrates the relationship between nitrate photolysis and atmospheric

Table 2 Photolysis rate constants of pNO_3^- (s) on various surfaces

Surface types	Conditions	Photolysis rate constants $J_{\text{HNO}_3} (\times 10^{-5} \text{ s}^{-1})$	Compared with the gas phase or liquid phase
Natural/artificial surfaces (Ye et al., 2016) (plant leaves, metal, building materials)	surface density of nitrate $0.4\text{--}28.0 \times 10^{-6} \text{ mol/m}^2$	0.6–15.3	1–3 orders of magnitude higher than the photolysis rate constants in gas phase or liquid phase
Titanium dioxide (Dyson et al., 2021)	$295 \pm 3 \text{ K}$, $\lambda = 290\text{--}400 \text{ nm}$	32.9	50 times higher than photolysis rate constants in the gas phase
Beijing, China Atmospheric particulate matter (Bao et al., 2018)	average value of samples collected over 15 d, 298 K, RH 60 %, simulated sunlight	11.67	1–3 orders of magnitude higher than photolysis rate constants in the gas phase
Albany, NY, USA Atmospheric particulate matter (Ye et al., 2017b)	293 K, RH 50 %, $\lambda > 290 \text{ nm}$, concentration of pNO_3^- $1.5\text{--}36.8 \times 10^{-9} \text{ mol/m}^3$	1.0–13.0	2 orders of magnitude higher than photolysis rate constants in the gas phase
Delmar, NY, USA Atmospheric particulate matter (Ye et al., 2017b)	293 K, RH 50 %, $\lambda > 290 \text{ nm}$, concentration of pNO_3^- $7.5\text{--}8.1 \times 10^{-9} \text{ mol/m}^3$	6.1–17.0	2 orders of magnitude higher than photolysis rate constants in the gas phase

**Fig. 4** Photolysis rate constants and lifetimes of nitrates in different phases (Reprint from (Ye et al., 2017b) with permission from the American Chemical Society).

lifetime in different phases (Ye et al., 2017b). $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ have shorter atmospheric lifetimes, which are in the range of 0.1 to 100 hours. Therefore, the contribution of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ photolysis to renoxification is more important than that of gaseous HNO_3 and $\text{NO}_3^-(\text{aq})$ in the liquid phase. The consideration of $\text{pNO}_3^-/\text{HNO}_3(\text{s})$ photolysis in current atmospheric chemistry mechanisms improves the simulations of reactive nitrogen chemistry in regional and global models. However, the specific mechanisms of the photolysis of particulate nitrate are still unclear and further research is needed in the future.

6 Summary, recommendations, and outlook

Fig. 5 summarizes the photolysis mechanisms of nitrate. The direct photolysis mechanism involves photoinduced cleavage of the N–O bonds, photoisomerization, and reactions between the photolytic fragments. The indirect

photolysis mechanism involves photosensitization and cleavage of the N–O bands. Photon absorption, proton transfer processes, and electron transfer processes are important factors determining the mechanism of nitrate photolysis.

Nitrate is one of the main components of atmospheric particulate matter, and the concentration of nitrate aerosol is closely related to regional air quality. In the USA, Europe, and other places where the air pollution from fine particulate matter is relatively low, the annual average concentration of pNO_3^- is $0.2\text{--}3.0 \mu\text{g/m}^3$ (Blanchard et al., 2007; Xing et al., 2015). In North China, the average concentration of pNO_3^- can reach $16.0\text{--}87.2 \mu\text{g/m}^3$, accounting for 10.4 %–29.9 % of $\text{PM}_{2.5}$ (Wen et al., 2015; Xu et al., 2016; Jiang et al., 2017). In recent years, the proportion of nitrate aerosols in atmospheric particulates has shown an upward trend. Several studies have shown that the relative content of sulfate decreased by about 10 %–50 %, and the relative content of nitrate increased by about 7 %–25 % in the aerosol particles in the North China Plain and the Sichuan Basin (China) from 2006 to 2017 (Spindler et al., 2013; Xu et al., 2019; Wang et al., 2020; Cheng et al., 2022), which suggests that nitrate plays an increasingly important role in the process of air pollution. The photolysis of HNO_3 /nitrate is indispensable in the process of air pollution and will initiate a series of reactions in the particulate phase (such as nitration for browning atmospheric aerosol). For these reactions and their environmental effects, we refer readers to the recent review (Gen et al., 2022). In this review, we focus on the effects of nitrate photolysis on atmospheric models, chemistry, and the local chemical environment. The photolysis of HNO_3 /nitrate can produce NO_x and HONO and affect the process of nitrate recycling and the regional atmospheric chemical process as follows.

First, the photolysis of HNO_3 /nitrate can explain the

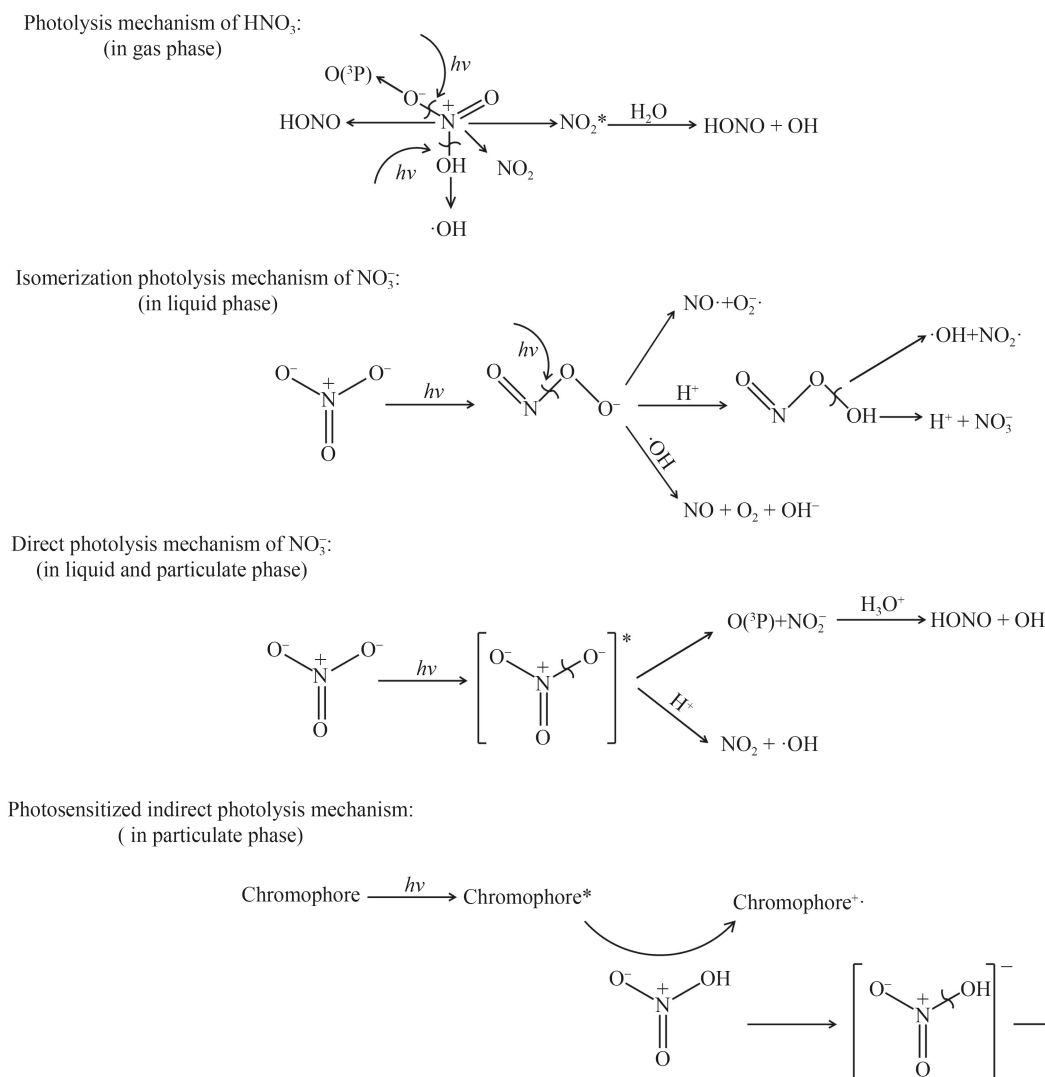


Fig. 5 Photolysis mechanisms of nitrate.

differences in HNO_3 concentrations between field measurements and model simulations. In the early research, a large difference existed between HNO_3 observations and model simulations. Models tended to overestimate the concentration of HNO_3 such that the predicted ratio of NO_x/HNO_3 was 5 to 10 times smaller than the observed values (Perkins et al., 2001; Rivera-Figueroa and Finlayson-Pitts, 2003). Model simulation results using modified rate constants of gas-phase reactions (such as $\text{OH}+\text{NO}_2$ and $\text{OH}+\text{HNO}_3$) could reduce the gap, but it was still difficult to match the observed ratios of NO_x/HNO_3 (Gao et al., 1999; Perkins et al., 2001). This suggested that unknown pathways of HNO_3 loss were missing from the current chemical mechanisms. The photolysis of HNO_3 and the heterogeneous reaction of HNO_3 with gaseous species (such as NO and CO) were considered to be two possible mechanisms. An early model study suggested that the heterogeneous reaction between CO and HNO_3 could

well reproduce the measured ratio of NO_x/HNO_3 (Lary and Shallcross, 2000). However, later laboratory experimental results showed that the heterogeneous reactions of CO , CH_4 , SO_2 and NO with HNO_3 under ambient atmospheric conditions were not important in the troposphere (Rivera-Figueroa and Finlayson-Pitts, 2003; Kleffmann et al., 2004). Therefore, the photolysis of nitrate may be an important factor affecting the concentration of atmospheric HNO_3 .

Second, the photolysis of $\text{HNO}_3/\text{nitrate}$ may explain the differences in HONO concentrations between field measurements and model simulations. HONO is an important precursor of OH radicals in the troposphere. OH radicals produced by HONO photolysis in the troposphere account for 20 %–80 % of the total OH radicals in the troposphere (Acker et al., 2006; Elshorbany et al., 2010). Several studies have shown that the measured daytime HONO concentration is greatly different from the modeled concentration based on the

known gas-phase chemical mechanism, with a difference of about 49 %–86.4 % (Kleffmann, 2007; Huang et al., 2017; Liu et al., 2021). Field observations also suggested the existence of unknown HONO sources (Zhang et al., 2009; Li et al., 2014). The photolysis of $\text{pNO}_3^-(\text{s})$ and the heterogeneous photoreaction of NO_2 on aerosols are considered two potential sources of daytime HONO (Kleffmann, 2007; Huang et al., 2017; Ye et al., 2017b; Bao et al., 2018). Nevertheless, current modeling results indicate that the contribution of $\text{pNO}_3^-(\text{s})$ photolysis to daytime HONO sources may only be important under certain environmental conditions (Sörgel et al., 2011; Oswald et al., 2015). For example, it was suggested that the contribution of $\text{pNO}_3^-(\text{s})$ photolysis to unknown diurnal HONO sources is high in remote, suburban, and rural areas with low NO_x concentrations, but low in urban environments with high NO_x concentrations (Ye et al., 2017a; Ye et al., 2017b; Tsai et al., 2018). Therefore, the specific contribution of $\text{pNO}_3^-(\text{s})$ photolysis to the unknown HONO source in the daytime and specific environmental conditions are worth exploring and further research.

Third, the photolysis of HNO_3 /nitrate can be involved in other chemical processes such as the oxidation of SO_2 to sulfate, formation of secondary organic aerosols (SOA) and formation of Cl_2 . The photolysis of nitrate can produce oxidants such as NO_2 , OH radicals, and N(III) ($\text{NO}_2^-/\text{HNO}_2$), which play a potential role in improving the atmospheric oxidative capacity. Sulfite or bisulfite in aerosol liquid water can be oxidized to sulfate by NO_2 , OH radicals or N(III) formed in the photolysis of nitrate, which could be important formation pathways during the haze event (Gen et al., 2019a,b). For example, a model work showed that the enhanced effect of $\text{pNO}_3^-(\text{s})$ photolysis on the heterogeneous oxidation of SO_2 could explain 15 % to 65 % of the difference in sulfate concentrations between model simulations and field observations during winter haze in Beijing (China) (Zheng et al., 2020). The contribution mainly depends on the enhancement of the photolysis rate constant of $\text{pNO}_3^-(\text{s})$ in aerosol. Nitrate photolysis was also found to enhance the formation of SOA in the oxidation of organic compounds. The OH radicals produced by the photolysis of nitrates can oxidize organic compounds in aerosol to form dimers or oligomers with low volatility, which are finally converted into SOA in particulate phase. Besides, recent field and laboratory experiments indicate that $\text{pNO}_3^-(\text{s})$ photolysis by sunlight under acidic conditions ($\text{pH} < 3.0$) can activate chloride to produce Cl_2 , which can account for the observed daytime Cl_2 production (Peng et al., 2022). This research suggests that nitrate photolysis is a significant daytime chlorine source globally and has an active effect on atmospheric oxidative capacity. Thus, the photolysis of $\text{pNO}_3^-(\text{s})$ can significantly contribute to the secondary formation of atmospheric active species and pollutants, and more

detailed mechanisms of SO_2 and organics oxidation are referred to this review (Gen et al., 2022).

Finally, the photolysis of HNO_3 /nitrate can lead to the transmission of NO_x with particulate matter and affect the distribution of NO_x . Ye et al. (2017a) used a zero-dimensional box model to study the effect of photolysis of pNO_3^- on NO_x and O_3 abundances in the remote marine boundary layer (MBL) of Cape Verde. Their results show that a model with the addition of the photolysis process of pNO_3^- can better reproduce the measured NO_x and O_3 levels. It is suggested that NO_x may be transported over long distances through the photolysis process of pNO_3^- , and may affect regional NO_x levels and atmospheric chemistry.

Several recommendations are made for future research.

Improve experimental conditions to simulate a more realistic tropospheric environment. Previous studies mainly focused on model nitrates (such as KNO_3 and NH_4NO_3) or HNO_3 rather than real particulate matters. Although several studies have conducted photolysis experiments on real $\text{PM}_{2.5}$, the nitrate samples are usually in an adsorbed state rather than a suspended state as exists in the atmosphere. Differences in photolysis rate constants due to particle dispersion and their reasons are not clear. More laboratory studies are necessary to investigate the photolysis of nitrate under more realistic tropospheric environmental conditions.

The specific mechanisms of nitrate photolysis. Many factors have been shown to enhance nitrate photolysis. However, most of the specific mechanisms of these enhancements are still at the level of conjecture and theory, lacking experimental evidence. A deeper study of photolysis mechanisms at the molecular level and theoretical calculation can deeply understand the theoretical basis behind nitrate photolysis. It is necessary to use advanced techniques (such as intermediate measurements and surface science techniques) to further research.

The specific contribution to unknown HONO and NO_x sources. The photolysis of nitrate can produce HONO and NO_x and has the potential to contribute to unknown diurnal sources of HONO and NO_x . However, the contribution of nitrate photolysis to HONO and NO_x source has great uncertainty due to different environmental conditions. The specific contribution of nitrate photolysis to missing HONO and NO_x sources in the daytime is also unclear. It is still necessary to conduct relevant experiments and further research with model simulations.

Impact on regional atmospheric chemistry. Nitrate may participate in other reaction processes during photolysis and alter the atmospheric oxidative capacity. Long-distance transmission and nighttime accumulation of nitrate may change the regional atmospheric chemistry and HONO- NO_x distribution during the day and night. Besides, ozone pollution has become an important

problem in China, and NO_x produced by photolysis of HNO_3 /nitrate in the atmosphere is a key precursor of ozone. Therefore, the effect of photolysis of HNO_3 /nitrate on ozone formation could be an important research issue in the future.

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