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Photoenhanced uptake of NO_2 on mineral dust: Laboratory experiments and model simulations

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[1] Mineral dust contains material such as TiO_2 that is well known to have photocatalytic activity. In this laboratory study, mixed TiO_2-SiO_2, Saharan dust and Arizona Test Dust were exposed to NO_2 in a coated wall flow tube reactor. While uptake in the dark was negligible, photoenhanced uptake of NO_2 was observed on all samples. For the mixed TiO_2-SiO_2, the uptake coefficients increased with increasing TiO_2 mass fraction, with BET uptake coefficients ranging from 0.12 to 1.9 $\times$ 10^{-6}. HONO was observed from all samples, with varying yields, e.g., 80% for Saharan dust. Three-dimensional modeling indicates that photochemistry of dust may reduce the NO_2 level up to 37% and ozone up to 5% during a dust event in the free troposphere. **Citation:** Ndour, M., B. D'Anna, C. George, O. Ka, Y. Balkanski, J. Kleffmann, K. Stemmler, and M. Ammann (2008), Photoenhanced uptake of NO_2 on mineral dust: Laboratory experiments and model simulations, *Geophys. Res. Lett.*, *35*, L05812, doi:10.1029/2007GL032006.

1. Introduction

[2] Following erosion from the ground, dust particles are mobilized by strong winds. Their chemical composition reflects that of the crustal materials from which they are produced. A typical composition is 60% SiO_2 and 10–15% Al_2O_3 (by weight) [*Usher et al.*, 2003]. Beside these major elements, some other oxides are found. The percentages of these other oxides, namely Fe_2O_3, MgO, CaO and TiO_2, are slightly more variable and dependent on source location. For instance, titanium dioxide (TiO_2) is found in dust particles at mass mixing ratios ranging from 0.1 to 10% depending on the exact location from where the particles were uplifted [*Hanisch and Crowley*, 2003]. It has been shown that the uptake of HNO_3 on dust has a significant effect on the global ozone budget [*Bauer et al.*, 2004].

[3] Both titanium and iron oxides are used as photochemical sources of radicals. Iron oxides are used to induce the so-called Fenton or Photo-Fenton reactions [*Deguillaume et al.*, 2005]. Pure TiO_2 is used in a variety of remediation processes due to its photocatalytic properties. The resulting free-radicals are very efficient oxidizers of organic and inorganic matter. For instance, pure TiO_2 has been demonstrated to be an effective photocatalyst for NO_2 reduction [*Gustafsson et al.*, 2006; *Yumoto et al.*, 2002]. It has also been suggested that TiO_2 present in fly ash particles may represent a sink of halocarbons in the troposphere [*Kutsuna et al.*, 1999]. However, the role of mineral dust aerosol as a photochemically active substrate that can modify the chemistry of the dust particles and their potential impact on the tropospheric composition has not been explored so far. Therefore, we investigated the effect of UV/visible light on the uptake kinetics of NO_2 on various mineral surfaces including SiO_2/TiO_2-based proxies and authentic dust particles.

2. Experimental

2.1. Horizontal Coated Wall Reactor

[4] The experiments were performed in a 20 cm $\times$ 1.05 cm (i.d.) thermostated horizontal coated wall reactor, detailed by *George et al.* [2005], fitted with four halogen lamps (OSRAM Halostar starlite, 50 W) with an irradiance of 0.069 mW cm^{-2} below 400 nm inside the reactor. With gas flows of ca. 850 mL min^{-1}, no gas phase photodissociation of NO_2 was observed. NO_2 was introduced into the reactor via a movable injector and monitored at the reactor exit with a NO_x chemiluminescence analyzer (THERMO 42C), which inlet was mounted with a carbonate denuder. The NO_2 uptake coefficients were determined by monitoring the loss of gas phase NO_2 as a function of time and exposed solid surface.

[5] Another set-up was run at lower NO_2 concentrations and higher irradiance using real mineral samples i.e., Arizona test dust and grinded Saharan sand. In this case, the irradiations of mineral dust substrates were performed using a slightly different experimental layout i.e., in a 50 cm $\times$ 0.8 cm (i.d.) Duran glass tubes installed in an air cooled lamp housing holding 7 fluorescence lamps (44 cm $\times$ 2.6 cm o. d.), in a circular arrangement surrounding the thermostated reactor tube. These experiments were performed with UV lamps (300–420 nm, 13.4 mW cm^{-2}).

[6] The measurements are reported in terms of the dimensionless uptake coefficient (γ), which simply defines the probability that a gas kinetic collision of a molecule on the surface leads to chemical conversion. γ is related to the measured first order rate coefficient k_w by:

$$k_W = \frac{\gamma_{geom}\langle C\rangle}{2r_{tube}} \quad (1)$$

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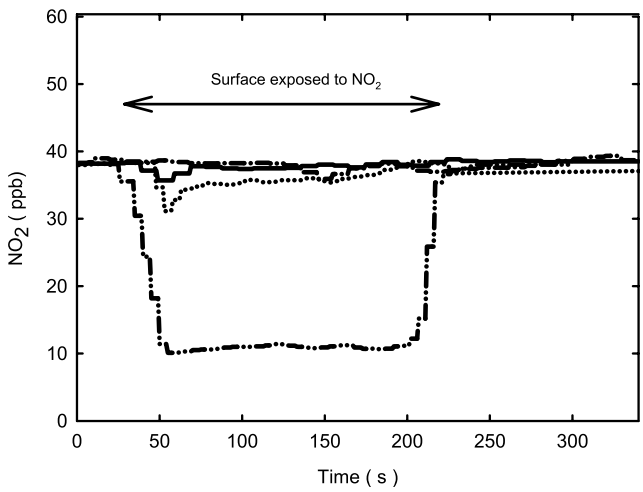

Figure 1. The data shown correspond to the NO_2 gas phase concentration at the exit of the flowtube after being exposed for 0.96 s to solid surfaces of SiO_2 (solid line in the dark and dash-dotted line, irradiated) and a TiO_2/SiO_2 (dotted in the dark and dash-dot-dotted line, irradiated) in the dark and irradiated by the four halogen lamps.

r_{tube}, γ_{geom} and $\langle c \rangle$ are the flow tube radius, geometric uptake coefficient and thermal molecular velocity, respectively. The mass-dependent γ_{geom} can be converted to a mass-independent γ_{BET} by taking into account the entire BET surface area of the sample instead of its geometric surface. All uptake coefficients reported below were obtained by considering the measured BET surface and were corrected for gas phase diffusion limitations.

[7] An indirect detection of the produced HONO was made by means of a NO/NO_x-chemiluminescence detector, in combination with a sodium carbonate denuder tube for removing HONO from the gas stream. In addition a direct HONO detection was made by using the LOPAP device (Long Path Absorption Photometer) [*Heland et al.*, 2001].

[8] The various mineral oxide powders investigated, SiO_2 (DEGUSSA Aerosil 130) and TiO_2 (DEGUSSA, P25 80% anatase, 20% rutile; P25), were purchased from Degussa. TiO_2 and SiO_2 (0.5–2 g) powder was dissolved in 20 ml of water and was dripped uniformly into the Pyrex flow tube and dried overnight in an oven at 100°C. The resulting film covered the entire inner area of the tube and, to the eye, was fairly uniform in thickness. Saharan sand was collected from the south of Mauritania (Tagant) and was grinded. Arizona Test Dust (Ultrafine Grade A1, Ellis Components, Stonebroom, UK), was also used [*Vlasenko et al.*, 2005]. Some samples were also analyzed for anions by means of ion chromatography (Dionex 120 equipped with an IonPac AS14A-4-mm column).

2.2. LMDz General Circulation Model

[9] The LMDz version used in this study has a horizontal resolution of 3.8 degrees in longitude and 2.5 degrees in latitude over the whole globe. INteraction with Chemistry and Aerosols (INCA) is coupled on-line to the LMDz general circulation model. INCA prepares the surface and *in situ* emissions, calculates dry deposition and wet scavenging rates, and integrates in time the concentration of atmospheric species with a time step of 30 min. The INCA-NMHC version 5 applied in this study is based on an earlier version which was developed to represent the background chemistry of the troposphere [*Hauglustaine et al.*, 2004].

[10] 43 photolytic reactions, 217 thermochemical reactions, and 5 heterogeneous reactions are taken into account by the model. The set of reactions and reaction rates are based on the scheme of *Brocheton et al.* [1999]. All reaction rates have been reviewed and updated with respect to the IUPAC and JPL compilations.

3. Results

[11] In the present study, solid TiO_2 diluted in SiO_2 at a mass mixing ratio of 1 wt% was used to mimic mineral dust at a relative humidity of 25%, consistent with those effectively reported for dust particles. For photoinduced processes, the uptake coefficients were normalized to the measured average irradiance I according to:

$$\Gamma_{phot} = \frac{\gamma_{BET}}{I} \tag{2}$$

In this case, the photochemical uptake coefficient Γ_{phot} has units of $(\text{mW cm}^{-2})^{-1}$. During these experiments, I was equal to 0.069 mW.cm^{-2} below 400 nm, i.e., in the wavelength range where TiO_2 can be photochemically activated. From Γ_{phot}, it becomes possible to estimate, assuming a constant quantum yield below 400 nm, the order of magnitude of the uptake coefficient at different irradiance. These uptake coefficients were implemented in the LMDz-INCA chemistry-climate model to evaluate the environmental significance of the reaction.

[12] The "dark" uptake of NO_2 has been observed, in agreement with previous studies, to be very low on all mineral solid surfaces exhibiting a time dependence with uptake coefficients γ_{BET} of ca. 10^{-9} at long reaction times. Such steady state uptake coefficients are in agreement with initial uptake coefficients reported by *Underwood et al.* [2001]. Without irradiation, no significant reaction was observed and under those conditions, as previously reported, the uptake of NO_2 on dust needs to be regarded as non significant.

[13] However, once the solid sample is irradiated a very rapid chemical conversion is observed. Figure 1 shows the raw data (dark and light) for an uptake experiment on a surface made of SiO_2 and TiO_2/SiO_2 at 1 wt% of TiO_2 when the Pyrex flowtube was irradiated with the halogen lamps. It is obvious that under irradiation, the uptake of NO_2 is driven by a fast chemical reaction on the solid film. In this case, the uptake of NO_2 has been photo-enhanced by ca. two orders of magnitude. Not only is the uptake rate drastically accelerated but it also appears is to be catalytic in the sense that (as shown in Figure 1) it does not depend on time, i.e., no surface saturation has been observed on these synthetic samples over hours (even at NO_2 concentrations as large as 300 ppb). The measured uptake coefficients were observed to be strongly dependent on the NO_2 gas phase concentrations, in the range from 7 to 380 ppb, as shown in Figure 2. This behavior can be explained via a Langmuir-Hinshelwood mechanism.

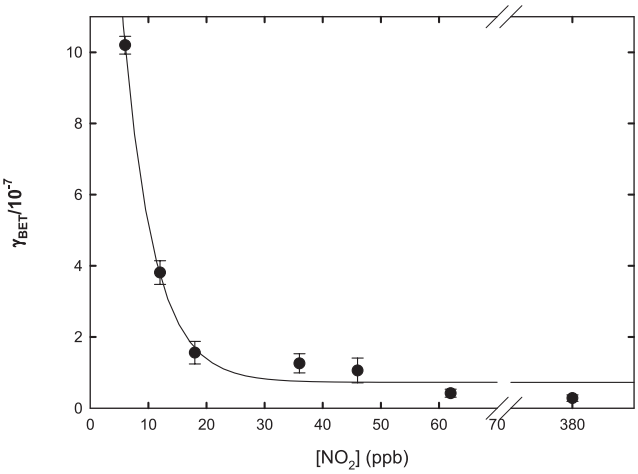

Figure 2. Dependence of the uptake coefficient as a function of the NO_2 gas phase concentration. All experimental were conducted at 298 K, m(dust) = 25.3 mg, and 25% relative humidity. Each point was obtained from measurements on fresh samples.

[14] Clearly these experiments on synthetic dust samples have demonstrated that under relevant atmospheric conditions mineral dust photochemistry should be considered as an important chemical pathway since the uptake coefficients (derived on the BET surface) were observed to be close to 10^{-6}, up to two orders of magnitude larger than without light. *Gustafsson et al.* [2006] derived the uptake rate of NO_2 onto pure TiO_2 to be ca. 8×10^{-3} with a higher irradiance than used here. Taking the different light intensity into account and normalizing our uptake rate solely to the TiO_2 surface, both data sets are in good agreement.

[15] Nevertheless, we ensured that these photolytic chemical conversions also occur under even more realistic conditions. This was performed at very low NO_2 concentrations, under realistic irradiation using real mineral samples i.e., Arizona test dust and grinded Saharan sand. As shown in Figure 3 both samples do cause photochemical conversion of NO_2 once irradiated.

[16] Arizona test dust is known to have a very small content of TiO_2 (below 1 wt%) while Saharan sand may have large variable contents of the oxide [*Hanisch and Crowley*, 2003; *Karagulian and Rossi*, 2005]. On synthetic samples, we observed that the photochemical uptake coefficient γ_{BET} increases from 0.12 to 1.9×10^{-6} with increasing TiO_2 content from 1 to 5 wt%.

[17] The photocatalytic action of TiO_2 is initiated by the photo-production of excess electrons in the conduction band (e^-_{cb}) and holes in the valence band (h^+_{vb}). The electron reduces the oxygen contained in the gas flow or the nitrogen dioxide while the hole oxidizes water vapor that is also present in the gas flow. The associated reactions mechanism could be [*Hoffmann et al.*, 1995]:

$$\mathrm{Dust(TiO_2)} + h\nu \rightarrow h^+_{vb} + e^-_{cb} \quad (3)$$

$$h^+_{vb} + H_2O \rightarrow OH + H^+ \quad (4)$$

$$e^-_{cb} + O_2 \rightarrow O_2^- \quad (5)$$

where the electrons, O_2^- and OH can react with nitrogen dioxide according to:

$$NO_2 + OH \rightarrow HNO_3 \quad (6)$$

$$NO_2 + O_2^- \left(\text{or } e^-_{cb}\right) \rightarrow NO_2^- + O_2 \quad (7)$$

It must be underlined that these reactions are just a subset of a large number of possible reactions altering the final yield of each product. Depending on the acidity of the surface, the production of nitrite anions is linked to that of gaseous nitrous acid (HONO), known to be a very important source of hydroxyl radicals. Nitrous acid may accumulate during night-time before undergoing photolysis in the morning, but may also be produced during daytime with strong photo-

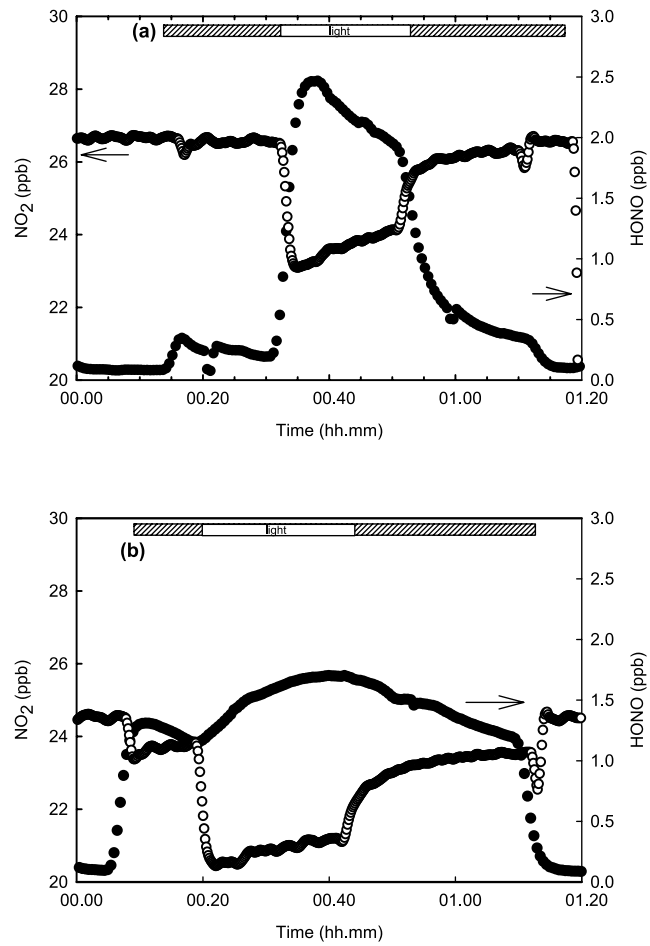

Figure 3. Conversion of NO_2 into HONO on UV-A (300–420 nm) irradiated mineral dust in presence of 24 ppb NO_2 and 24% relative humidity. (a) The formation of HONO (solid circles, right axis) and the removal of NO_2 (open circles) on a 32 mg deposited Saharan dust. (b) The formation of HONO (solid circles, right axis) and the removal of NO_2 (open circles) on a 56 mg deposited Arizona Test dust. The grey area at the top of the panels indicates the periods during which the film was exposed to NO_2 in the dark, the yellow area indicates the time when the film was irradiated.

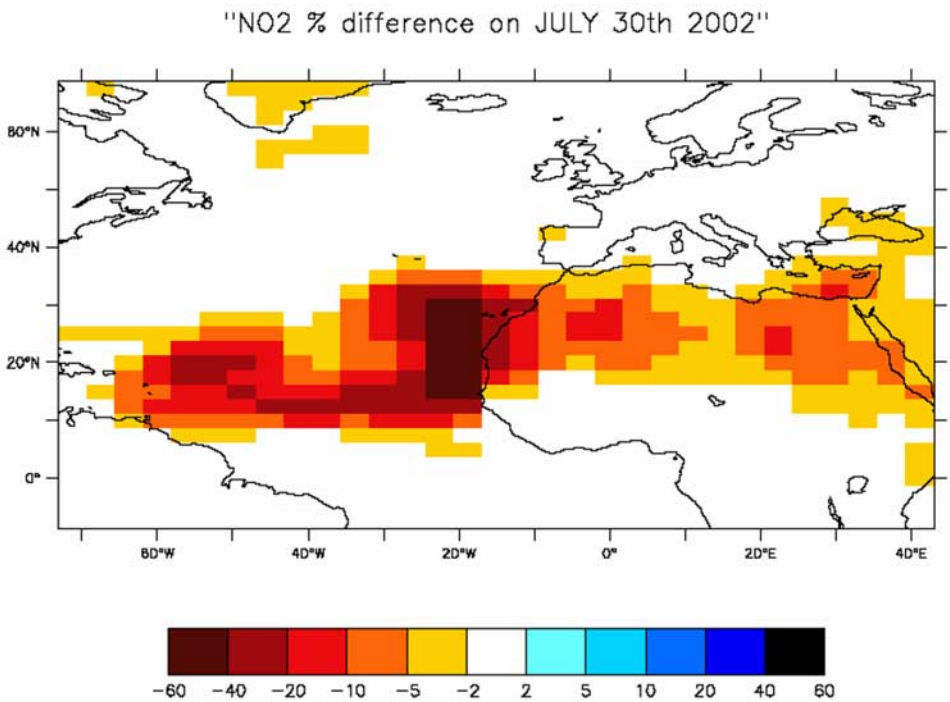

Figure 4. Percentage change in free tropospheric NO_2 concentration during a dust episode that occurred on July 30, 2002 over the Western Sahara, due to photochemically enhanced uptake on dust.

chemical sources of 200–1800 pptv/h up to 60 times faster than all night-time sources [*Kleffmann et al.*, 2007].

[18] On the synthetic dust samples, an indirect identification of acidic gases such as HONO was made by connecting or disconnecting a potassium carbonate denuder at the inlet of the NO/NO_x-chemiluminescence detector. Using this procedure, HONO was observed to be produced solely when the solid surfaces were irradiated. On synthetic dust surfaces (i.e., 1 wt. % TiO_2 in SiO_2) HONO was produced with an average yield of 33% in experiments with 420 ppb of NO_2. This yield is smaller than the one reported by [*Gustafsson et al.*, 2006] (i.e., 75%) on pure TiO_2. This difference could be explained by different surface characteristics of the samples used. In addition, HONO was unambiguously detected under realistic conditions using Arizona test dust or grinded Saharan sand exposed to 24 ppb NO_2 (see Figure 3) by means of the LOPAP instrument, which selectively detects HONO. For the grinded Saharan sand sample, O., the HONO yield is about 80%. For the Arizona test dust, the yield was lower and a delayed emission of HONO was observed, indicating that surface acidity, microstructure and other factors control the release of HONO in real dust samples, while the loss of NO_2 was remarkably similar. Photochemical HONO formation was observed for the first time on real surfaces and not only on synthetic TiO_2 samples. Nitrate anions were also observed to be solely produced during the photoconversion of NO_2 on dust.

[19] Runs with the LMDz-INCA model shown in Figure 4 demonstrate the effect of photochemical conversion of NO_2 on dust into HONO and nitrates on the NO_2 concentrations during a dust episode that occurred during summer 2002 over the western Saharan, documented during the second phase of MINATROC 2 [*de Reus et al.*, 2005; *Umann et al.*, 2005]. For the simulations, a Γ_{phot} value of 1.48 10^{-5} mW cm^{-2}, determined for low NO_2 concentration on SiO_2/TiO_2 surfaces, was considered. The simulated NO_2 concentrations decrease by 37% in the free troposphere in regions as the optical depth of the dust cloud averages 0.5 at 550 nm. Coincidently, nitric acid and OH decrease by 54.0 and 9.2% respectively, over the same region (see Table 1). The decreases in these photochemical species lead to a simulated O_3 concentration decrease of 5.1%.

[20] When averaged over the globe, the decrease in simulated NO_2 concentrations in the free troposphere amounts to 3.0%. For nitric acid, OH and O_3, the respective decrease averaged over the month of July are: 8.4, 1.7 and 1.4%.

4. Conclusion

[21] In this study, by using NO_2 as a probe molecule, we demonstrated unambiguously, under atmospheric relevant conditions, that photochemistry of dust is important. Consequently, this new chemical pathway needs to be considered in forthcoming modelling studies in order to better assess the impact of dust on the atmospheric composition.

Table 1. Percentage Change and [Mix – Max Values] in NO_2, OH, HNO_3, and O_3 Concentrations During a Dust Episode on July 30, 2002, Over the Western Sahara Due to the Photochemical Reaction of NO_2 on Dust

	[28W–13W; 13N–34N] July 30, 2002	Global July Mean
NO_2	−36.6 [−56.8 to −3.4]	−3.0 [−22.7 to 0.3]
OH	−9.2 [−13.0 to −3.5]	−1.7 [−8.9 to −0.1]
HNO_3	−54.0 [−74.0 to −23.4]	−8.4 [−47.3 to −0.4]
O_3	−5.1 [−6.8 to −3.3]	−1.4 [−4.4 to −0.12]

Indeed, we note that apart from NO_2, which serves as electron acceptor, many other trace gas species or condensed constituents may be reduced or oxidized in a similar way on dust exposed to sunlight, potentially giving a wide impact of this photochemistry.

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