

Response to Reviewers' comments (Manuscript Ref. NO.: acp-2017-120)

We would like to thank the reviewer for the thoughtful comments. We have carefully studied these comments and made the corrections. The quality of this manuscript has been greatly improved due to the valuable suggestions.

Reviewer #1:

Overall Comment

This paper presents an interesting contribution aiming at the development of new numerical model of dust (photo)chemistry. It describes in some detail the different key process that are implemented. Clearly, the use of surface photochemistry is a novel and valuable contribution. However, a few aspects of this modelling studies are raising a few important questions.

Comment 1: The partitioning between the gas and condensed phase are treated in a similar way, despite being fundamentally different in nature. For a solid surface, the adsorption and desorption processes do follow a different formalism, typically through a Langmuir-Hinshelwood formalism which takes into account a given number of adsorption sites. The consequences is that adsorption decreases with time or increasing concentration, while here it is simulated in a constant way with time. how can you justify such an assumption? Also products such as sulfate are probably staying on the surface, thereby also using adsorption sites i.e., poisoning the surface. How would your model change if you implement such time/concentration dependence?

Response: We assumed that the gas-particle partitioning onto dust is operated by an absorption process (Eq. 7) by several reasons (see section 3.2.1). First, unlike pure metal oxide which is governed by the adsorptive partitioning, the composition of authentic mineral dust such as Arizona Test Dust (ATD) is complex. The fresh ATD contains inorganic salts that are hygroscopic and form the water film above efflorescence relative humidity or deliquescence relative humidity. Second, the partitioning process is dynamic due to the formation of various hygroscopic salts of sulfate and nitrate due to the reaction of alkaline carbonates and metal oxides with inorganic acids (sulfuric acid and nitric acid). Third, the sulfate formation in our study increased as increasing humidity due to the dissolution of tracers into the water layer (see section 3.2.1). If partitioning is processed by the adsorptive mode, water molecules compete for the site with tracers and reduce partitioning of tracers (Cwiertny et al., 2008). The amount of the surface water on dust particles, which was measured using FTIR (submitted in the other journal), was multi-layered.

Comment 2: Why having chosen to simulate deliquesced sea-salt and dust in the same code? What is the link between both objects/themes? Can you justify such a choice? Also the text mentions sea-salt and the partitioning process is described for aqueous sulfuric acid particles. Please harmonize the different part of your manuscript.

Response: We have never mentioned about the deliquesced sea-salt in this study. For the formation of sulfuric acid in inorganic salted aqueous aerosol ($\text{SO}_4^{2-}\text{-NH}_4^+\text{-H}_2\text{O}$ system) (Section 3.1.3), we employed the aqueous phase kinetic reactions previously reported in literatures (Lee, 1984; Strehlow and Wagner, 1982; Gratzel et al., 1970; Graedel and Weschler, 1981; Treinin and Hayon, 1970; Lee and Lind, 1986; Damschen and Martin, 1983; Liang and Jacobson, 1999; Hoyle et al., 2016).

Comment 3: The characteristic time for adsorption is very different between aqueous and dust particles. Is this physically justified, bearing in mind that those processes are mostly related to gas phase and aerosols properties.

Response: The characteristic time of the uptake process of gas into aqueous phase or dust phase is calculated for gas-phase diffusion, liquid phase diffusion, establishing equilibrium at the interface and the reactions in gas, aqueous, and dust phases (Finlayson-Pitts and Pitts Jr, 1999). Table S2 has been added to supporting information in revised manuscript.

Table S2. The calculation of the characteristic time of the major processes and reactions

Type of process	Characteristic time	Aqueous phase system	Dust system
r : the particle radius D_g : diffusion coefficient in gas D_l : diffusion coefficient in aqueous phase H : Henry's constant α : the mass accommodation coefficient (0.5) u_{av} is the mean thermal speed.		$r = 50 \text{ nm}$ $k_{\text{SO}_2,g} = 1 \times 10^{-12} \text{ s}^{-1} \text{ molecule}^{-1} \text{ cc}$ $[\text{OH}] = 1 \times 10^6 \text{ molecules/cc}$ $k_{\text{HSO}_3} = 3 \times 10^{-3} \text{ s}^{-1} \text{ molecule}^{-1} \text{ cc}$ $[\text{OH}]_{\text{aq}} = 0.1 \text{ molecules/cc}$	$r = 350 \text{ nm}$ (average) $r_{\text{dust,aq}}$: the average thickness of the water layer on dust particles (40 nm) $k_{\text{SO}_2,g} = 1 \times 10^{-12} \text{ s}^{-1} \text{ molecule}^{-1} \text{ cc}$ $[\text{OH}] = 1 \times 10^6 \text{ molecules/cc}$ $k_{\text{SO}_2,\text{dust}} = 1 \times 10^{-12} \text{ s}^{-1} \text{ molecule}^{-1} \text{ cc}$ $[\text{OH}]_{\text{aq}} = 2 \times 10^9 \text{ molecules/cc}$
Gas diffusion	$\frac{r^2}{\pi^2 D_g}$	$2.4 \times 10^{-11} \text{ s}$	$2.1 \times 10^{-10} \text{ s}$
Diffusion in aqueous phase	$\frac{r_{\text{aq}}^2}{\pi^2 D_l}$	$1.9 \times 10^{-7} \text{ s}$	
Diffusion in the water layer on dust	$\frac{r_{\text{dust,aq}}^2}{\pi^2 D_l}$		$1.2 \times 10^{-7} \text{ s}$
Equilibrium between gas and particle	$D_l \left(\frac{4HRT}{\alpha u_{av}} \right)^2$	$7.1 \times 10^{-10} \text{ s}$	$7.1 \times 10^{-10} \text{ s}$
Reaction in gas phase	$\frac{1}{[\text{OH}]k_{\text{SO}_2,g}}$	$1 \times 10^6 \text{ s}$	$1 \times 10^6 \text{ s}$
Reaction in aqueous phase	$\frac{1}{[\text{OH}]_{\text{aq}}k_{\text{HSO}_3,\text{aq}}}$	$2 \times 10^3 \text{ s}$	
Reaction in dust phase	$\frac{1}{[\text{OH}]_{\text{dust}}k_{\text{SO}_2,\text{dust}}}$		$5 \times 10^2 \text{ s}$

For both the aqueous system and the dust system, the characteristic time of all reactions in gas and particles are much greater than diffusion in gas or particle phases and equilibrium processes (partitioning and dissociation of acids). Thus, the reactions of chemical species are not affected by the time reached to equilibrium or diffusion processes. In the model, both absorption and desorption rates of chemical species were set to much faster than their reaction rates in all three phase (last paragraph in Section 3.1.2). Furthermore, the time of diffusion in the liquid phase is longer than both gas diffusion and the time for reaching to equilibrium as shown in Table S2.

Comment 4: Too many rate constants are estimated without any justification. Please justify and explain your estimations.

Response: Most of the rate constants shown in Table 3 were estimated using the indoor chamber data obtained in the previous study (Park and Jang, 2016). The rate constants of R10 (electron-hole production) and R11 (recombination of electron-hole) in the manuscript is estimated using Eq. 10 (photoactivation rate, J_{ATD}) in the manuscript (Section 3.2.3). The rate constant of R13 (reaction of SO₂ with dust-phase OH radicals) is set to the same reaction rate constant for the reaction of SO₂ with OH radicals in gas phase. Without sunlight, autoxidation of SO₂ (R9) is dominant in dust phase and its rate constant was obtained from indoor chamber data under various humidity conditions (Exp. D1-D3 in Table 1). With sunlight, the photochemical reaction is the major source for sulfate production. Using the same approach with autoxidation, the rate constant of R12 was estimated under different humidity conditions. Also, the rate constants of R14 (heterogeneous autoxidation of SO₂ in the presence of ozone) and R15 (heterogeneous oxidation of O₃) were estimated using experiments D4 and L5 in Table 1, respectively. The rate constants of R18 (heterogeneous autoxidation of NO₂) and R19 (heterogeneous photocatalytic oxidation of NO₂) were estimated using experiments D5 and L7 in Table 1, respectively.

Comment 5: The agreement with the chamber data has to be described in a more quantitative way. By looking at the figures, one may have the impression that the agreement is not as good as described in the text.

Response: We agree with the reviewer. After carefully searching the errors, we found that mistakes in the estimation of the aerosol water content and aerosol acidity due to the incorrect input parameter for the titration of sulfuric acid with ammonia. The FS value, a numeric number to dynamically represent the composition of the sulfate-ammonium aerosol system, ranges from 0.34 (ammonium sulfate) to 1.0 (sulfuric acid). In the previous simulation, FS was computed sometimes at out of range due to the incorrect input of ammonia data. By the correction of this error, the model prediction in Fig. 3 were improved. In addition to the correction of input errors, we found some contamination in the NO₂ tank by nitric acid for the experiments with NO₂ (11/26/2015, 11/05/2016 and 11/22/2016). We conducted additional experiments with the new NO_x tank (Table 2 in the revised manuscript) and applied these new data to model evaluations (Figure 4 and Table 2 in the revised manuscript). The simulation of SO₂ oxidation in the presence of NO₂ was much improved.

Table 2. Outdoor chamber experiment condition for SO₂ heterogeneously photooxidation on the ATD particles at variety initial concentration of SO₂, dust particle and NO₂.

Exp. Date	Purpose	RH ^a (%)	Temp. ^a (K)	simulation Time (EST)	Initial Concentration ^b			
					ATD dust ^c ($\mu\text{g m}^{-3}$)	SO ₂ (ppb)	NO/NO ₂ (ppb)	O ₃ (ppb)
3/28/2015	SO ₂	18-67	277.1-301.9	11:10-16:30	N.A.	60.1	0.1/0.9	6.3
	SO ₂ & dust	24-71	277.8-301.5	10:50-16:30	290.1	56.4	0.1/0.7	0.7
6/16/2015	Low dust	15-49	286.7-313.0	8:40-15:30	90.1	100.0	0.1/0.7	0.7
	High dust	16-48	287.0-311.5	9:30-15:30	403.7	120.1	1.1/1.0	5
11/12/2015	Low SO ₂	24-71	277.8-301.5	8:40-17:30	239.2	119.0	0.5/2.0	3.0
	High SO ₂	14-42	296.2-325.0	9:00-17:30	229.0	271.6	0.2/2.1	2.6
04/14/2017	NO _x effect	33-95	287.8-314.3	6:30-17:30	496.2	88.1	88.9/13.5	3.0
04/25/2017-1	NO _x effect	18-89	283.8-313.6	6:00-16:00	414.0	15.0	112.0/13.2	2.2
04/25/2017-2	NO _x effect	26-94	284.1-312.7	6:00-16:00	478.7	17.5	35.9/3.6	1.9

^a The accuracy of RH is $\pm 5\%$. The accuracy of temperature is ± 0.5 K.

^b The errors associated with the observation of SO₂, NO, NO₂, O₃, NH₄⁺ and the concentration of dust particle mass were $\pm 0.9\%$, $\pm 12.5\%$, $\pm 6.9\%$, $\pm 0.2\%$, $5.0\pm\%$ and $\pm 6\%$, respectively. The detailed observations of the chemical species during the experiments were shown in Fig. S4 and Fig. S5 in Supporting Information.

^c The mass concentration of ATD particles were calculated combining SMPS data, OPC data, the density of dust particles (2.65 g cm^{-3}), and the particle size distribution ($< 3\mu\text{m}$).

Figure 3

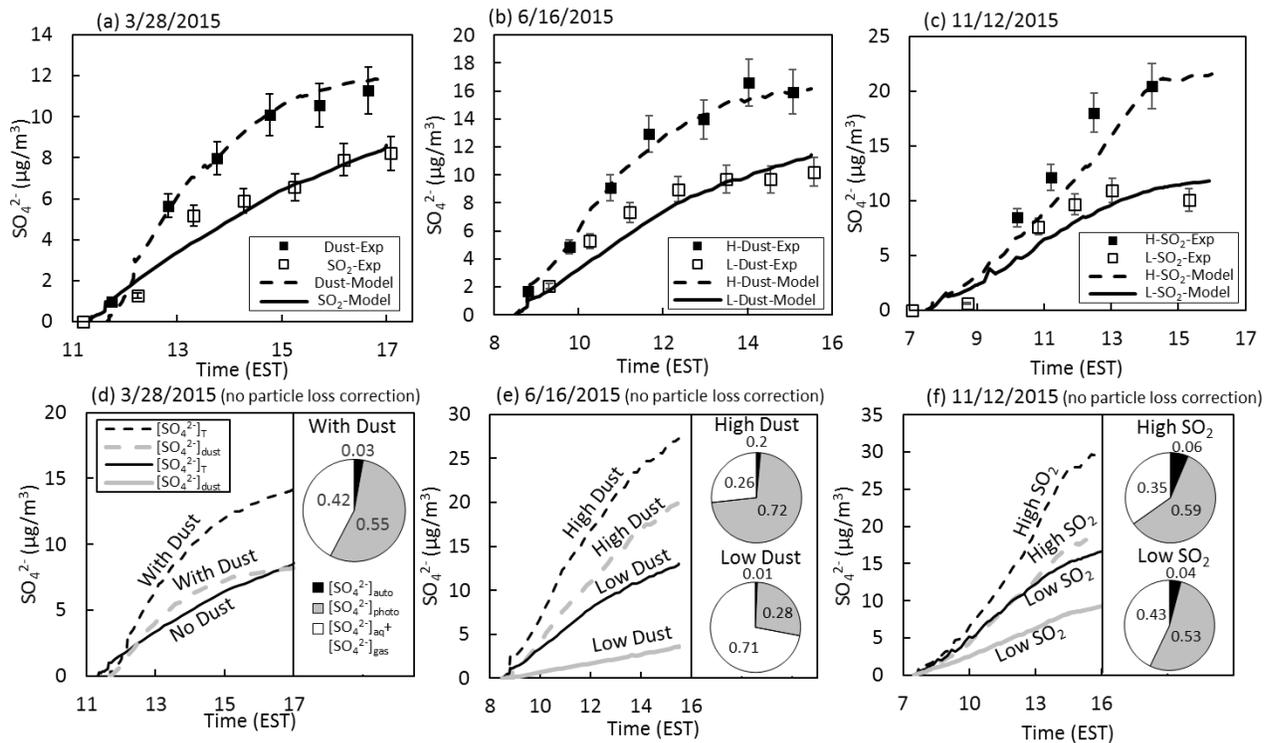


Figure 3. Time profiles of total sulfate concentration (SO_4^{2-} , $\mu\text{g m}^{-3}$) in the UF-APHOR. “Exp” denotes the experimentally observed sulfate ($[\text{SO}_4^{2-}]_{\text{T}}$) and “Model” denotes the model-predicted sulfate. “H” and “L” represent the high and the low initial concentrations of chemical species. (a) Sulfate formation with and without ATD particles (SO_2 60 ppb vs. SO_2 56 ppb and dust $290 \mu\text{g m}^{-3}$). (b) The high and low loadings of dust particles (dust $90 \mu\text{g m}^{-3}$ and SO_2 100 ppb vs. dust $404 \mu\text{g m}^{-3}$ and SO_2 120 ppb). (c) The high and the low concentrations of SO_2 (SO_2 119 ppb and dust $239 \mu\text{g m}^{-3}$ vs. SO_2 272 ppb and dust $230 \mu\text{g m}^{-3}$). For Fig. 3(a), 3(b) and 3(c), the simulations included the chamber dilution and the wall process of gaseous compounds and particles (Sect. S1). For Fig. 3(d), 3(e) and 3(f), the wall process for the particle loss was excluded to estimate the influence of ATD particles on sulfate formation without the chamber artefacts. In Fig. 3(d), 3(e) and 3(f), total sulfate was decoupled into the sulfate sourced from dust chemistry ($[\text{SO}_4^{2-}]_{\text{dust}}$). The pie charts inserted into Fig. 3(d), 3(e) and 3(f) illustrate how total sulfate is attributed to major pathways at the end of the experiments.

Figure 4

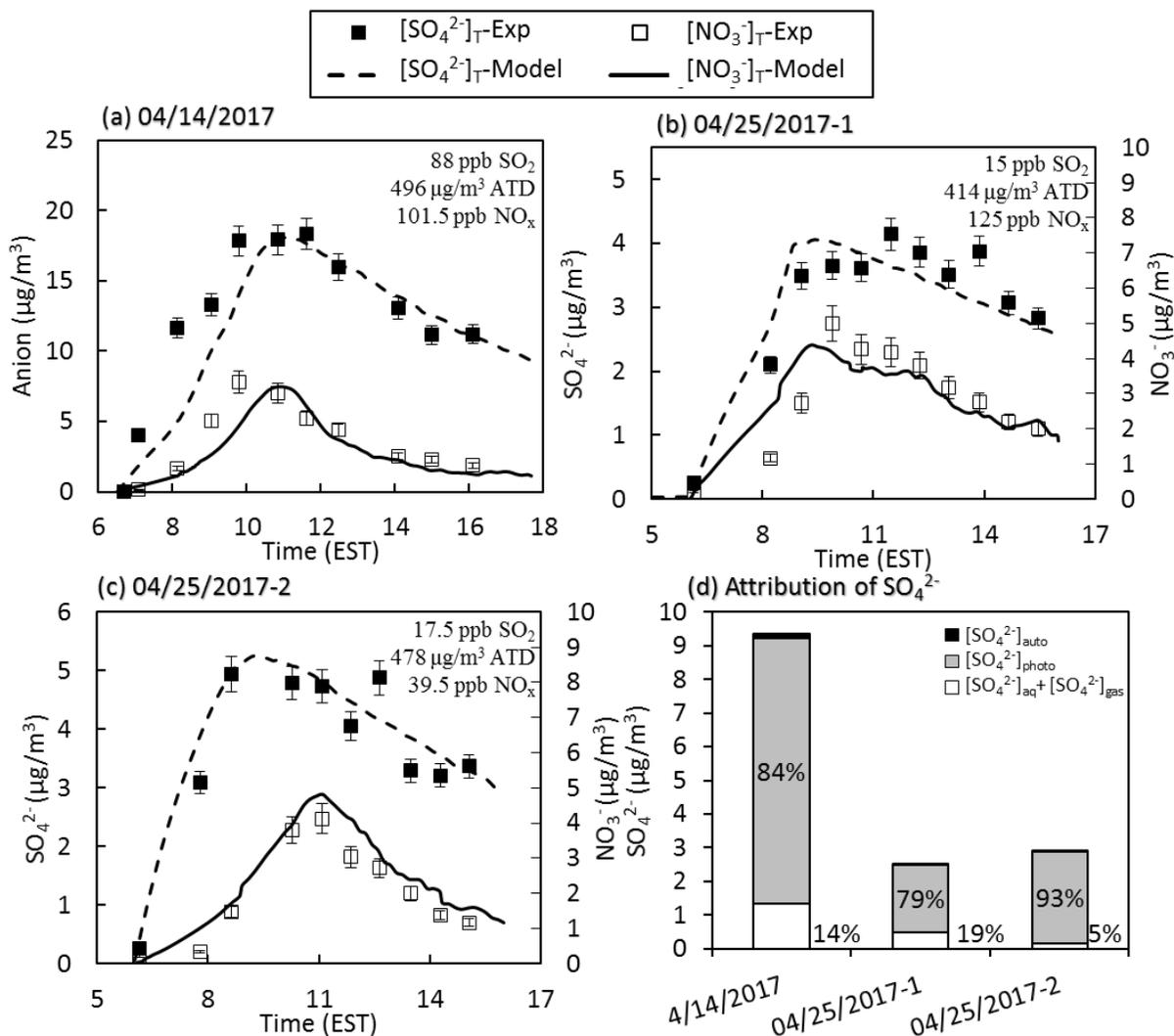


Figure 4. Time profiles of total sulfate concentration ($[\text{SO}_4^{2-}]_T$, $\mu\text{g}/\text{m}^3$) and nitrate concentration ($[\text{NO}_3^-]_T$, $\mu\text{g}/\text{m}^3$) in the dual chamber experiments using UF-APHOR at different NO_x levels. The concentrations of sulfate and nitrate were measured using PILS-IC during the experiments. The detailed experimental conditions of Fig. 4(a), Fig. 4(b), and Fig. 4(c) are shown in Table 2. Figure 4(d) shows how total sulfate is attributed to aqueous phase reaction (sulfate formation in gas phase + sulfate formation in inorganic salted inorganic aqueous phase) ($[\text{SO}_4^{2-}]_{\text{aq}} + [\text{SO}_4^{2-}]_{\text{gas}}$), dust-phase autoxidation ($[\text{SO}_4^{2-}]_{\text{auto}}$), and dust photochemistry ($[\text{SO}_4^{2-}]_{\text{photo}}$) at the end of the experiments. “Exp” denotes the experimental observation and “Model” denotes the simulation using the AMAR module. The chamber dilution and the wall process of gaseous compounds and particles were included in the simulation (Sect. S1).

Reference

- Cwiertny, D. M., Young, M. A., and Grassian, V. H.: Chemistry and photochemistry of mineral dust aerosol, *Annu Rev Phys Chem*, 59, 27-51, 10.1146/annurev.physchem.59.032607.093630, 2008.
- Damschen, D. E., and Martin, L. R.: Aqueous aerosol oxidation of nitrous acid by O₂, O₃ and H₂O₂, *Atmospheric Environment* (1967), 17, 2005-2011, 1983.
- Finlayson-Pitts, B. J., and Pitts Jr, J. N.: Chemistry of the upper and lower atmosphere: theory, experiments, and applications, Academic press, 1999.
- Graedel, T., and Weschler, C.: Chemistry within aqueous atmospheric aerosols and raindrops, *Rev Geophys*, 19, 505-539, 1981.
- Grätzel, M., Taniguchi, S., and Henglein, A.: Pulsradiolytische Untersuchung der NO-Oxydation und des Gleichgewichts $\text{N}_2\text{O}_3 \rightleftharpoons \text{NO} + \text{NO}_2$ in wäßriger Lösung, *Berichte der Bunsengesellschaft für physikalische Chemie*, 74, 488-492, 1970.
- Hoyle, C. R., Fuchs, C., Jarvinen, E., Saathoff, H., Dias, A., El Haddad, I., Gysel, M., Coburn, S. C., Trostl, J., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Corbin, J. C., Craven, J., Donahue, N. M., Duplissy, J., Ehrhart, S., Frege, C., Gordon, H., Hoppel, N., Heinritzi, M., Kristensen, T. B., Molteni, U., Niehman, L., Pinterich, T., Prevot, A. S. H., Simon, M., Slowik, J. G., Steiner, G., Tome, A., Vogel, A. L., Volkamer, R., Wagner, A. C., Wagner, R., Wexler, A. S., Williamson, C., Winkler, P. M., Yan, C., Amorim, A., Dommen, J., Curtius, J., Gallagher, M. W., Flagan, R. C., Hansel, A., Kirkby, J., Kulmala, M., Mohler, O., Stratmann, F., Worsnop, D. R., and Baltensperger, U.: Aqueous phase oxidation of sulphur dioxide by ozone in cloud droplets, *Atmos Chem Phys*, 16, 1693-1712, 10.5194/acp-16-1693-2016, 2016.
- Krueger, B. J., Grassian, V. H., Laskin, A., and Cowin, J. P.: The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, *Geophys Res Lett*, 30, Artn 1148 10.1029/2002gl016563, 2003.
- Lee, Y.-N.: Atmospheric aqueous-phase reactions of nitrogen species, Brookhaven National Lab., Upton, NY (USA), 1984.
- Lee, Y. N., and Lind, J. A.: Kinetics of aqueous-phase oxidation of nitrogen (III) by hydrogen peroxide, *Journal of Geophysical Research: Atmospheres*, 91, 2793-2800, 1986.
- Liang, J. Y., and Jacobson, M. Z.: A study of sulfur dioxide oxidation pathways over a range of liquid water contents, pH values, and temperatures, *J Geophys Res-Atmos*, 104, 13749-13769, Doi 10.1029/1999jd900097, 1999.
- Liu, Y. J., Zhu, T., Zhao, D. F., and Zhang, Z. F.: Investigation of the hygroscopic properties of Ca(NO₃)₂ and internally mixed Ca(NO₃)₂/CaCO₃ particles by micro-Raman spectrometry, *Atmos Chem Phys*, 8, 7205-7215, 2008.
- Park, J., and Jang, M.: Heterogeneous photooxidation of sulfur dioxide in the presence of airborne mineral dust particles, *RSC Advances*, 6, 58617-58627, 2016.
- Strehlow, H., and Wagner, I.: Flash photolysis in aqueous nitrite solutions, *Zeitschrift für Physikalische Chemie*, 132, 151-160, 1982.
- Treinin, A., and Hayon, E.: Absorption spectra and reaction kinetics of NO₂, N₂O₃, and N₂O₄ in aqueous solution, *J Am Chem Soc*, 92, 5821-5828, 1970.