

Interactive comment on “Effects of SO₂ on optical properties of secondary organic aerosol generated from photooxidation of toluene under different relative humidity” by Wenyu Zhang et al.

Anonymous Referee #1

Received and published: 19 August 2019

General comments:

The authors reported the effects of relative humidity and sulfur dioxide level on the optical properties of secondary organic aerosol from the toluene/NO_x photooxidation. Toluene is a representative anthropogenic aromatic hydrocarbon. Secondary organic aerosol from anthropogenic aromatic hydrocarbons comprises a portion of ambient organic aerosol particles at a global scale, and may affect the earth's climate. The optical properties of toluene secondary organic aerosol were already reported by several groups. However, a dataset reported in this manuscript is valuable because it is poorly understood on the effects of relative humidity and sulfur dioxide level on the optical

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properties of toluene secondary organic aerosol. In the current form, discussion will be insufficient on (1) discrepancy between present and previous results of the visible absorption of SOA formed under dry neutral conditions and (2) the effects of humidity and acidity on charge transfer complexes. Revisions are necessary for the publication.

Major comments:

(1) The authors reported that secondary organic aerosol formed under dry neutral conditions had little absorption at 375 nm. In contrast, several previous studies reported that toluene secondary organic aerosol formed under dry neutral conditions had visible absorption. Nakayama et al. (2010; 2013) reported that the imaginary refractive index (k) was 0.05 at 355 nm and 0.002 – 0.007 at 405 nm, where aerosol was formed at RH <1%. Zhong and Jang (2011) reported that k was 0.02 at 350 nm in the absence of seed particles, where aerosol was formed at RH = 42 – 43%. Liu et al. (2015) reported that k was 0.01 – 0.03 at 320 nm and 0.002 – 0.02 at 405 nm, where aerosol was formed at RH = 13%. The author should compare present results with these previous results to characterize present experimental conditions. The reviewer assumes that nitrophenols, light-absorbing substances formed during classical toluene/NO_x experiments, will barely be produced in their toluene/HONO/NO_x irradiation system due to high NO to NO₂ ratios during secondary aerosol formation.

(2) The authors suggest that visible absorption of secondary organic aerosol, formed in the toluene/NO_x/SO₂ irradiation system, was attributed to charge transfer complexes. They refer results of ambient aerosol collected in the winter season for the assignment of light-absorbing substances present in laboratory toluene secondary aerosol samples. The authors suggest that charge transfer complexes are formed between small alcohol and carbonyl molecules. However, reactions of alcohols with carbonyls in the condensed phase are enhanced under acidic conditions to result in the formation of hemiacetals. Furthermore, the reactions of carbonyls with aerosol water will lead to the formation of hydrated carbonyls, which cannot form charge transfer complexes with alcohols. It is widely accepted that the formation of hemiacetals and hydrated carbonyls

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occur during secondary organic aerosol formation (Jang et al., 2002). The formation of hemiacetals and hydrated carbonyls will suppress the formation of charge transfer complexes under humid and acidic conditions; this is inconsistent with present trends of k , which increased with increasing humidity and acidity. The authors should discuss the effects of humidity and acidity on chemical reactions between alcohols and carbonyls in the condensed phase and might need to tone down the identifications of charge transfer complexes as light-absorption substances.

(3) In line 33, page 4, the authors define RI as complex refractive index, $n + ik$. However, RI is often used as the real part of refractive index (n) in the latter part of the text. Please distinguish between RI and n through text. For example, all RIs used in eq. 4 and lines 8, 17, and 19 of page 6 must indicate the real part of refractive index. Also, “RRI” in line 29, page 6 must be the real part of refractive index. There will also be multi-definition RI symbols at other places.

(4) Line 35, page 6 and other places. The authors use the terminologies, “macromolecules” and “polymers,” for high molecular weight products from the oxidation of toluene. Generally, macromolecules and polymers are defined to be high molecular compounds in excess of 1,000 atoms (Staudinger and Fritschi, 1922), indicating that the molecular weight of macromolecules is higher than several thousands. On the other hand, the molecular weight is reported to be less than 1,000 for high molecular weight products formed from the toluene oxidation (Sato et al., 2007; Molteni et al., 2018). From this point of view, high molecular weight compounds detected in secondary organic aerosol particles are generally referred as oligomers. Please consider using “oligomers” instead of “organic macromolecules”, “macromolecular polymers”, or “macromolecular oligomers” for high-molecular weight products formed from the photooxidation of toluene.

(5) There are many minor grammatical errors through text. For example, “secondary organic aerosol (SOA) account for...” in line 2, page 2 should be “secondary organic aerosol (SOA) accounts for...”. In line 26, page 3, the description, “SMPS, which

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was consisted of . . .,” should be “SMPS, which consisted of . . .”. The reviewer does not point out all errors. The reviewer recommends the authors to use commercial English correction.

Specific comments:

(6) Line 12, page 4., What is “a total NO_x level” when a mixture of HONO, NO, and NO₂ is measured by a NO_x monitor? Please explain it explicitly. Is it a total level of pure NO_x (= NO + NO₂)?

(7) Line 14, page 4. The relative humidity was set to more than 80% during experiments under humid conditions. The reviewer believes that dew drops may appear on chamber wall under such high relative humidity conditions, and water soluble small organic compounds will be dissolved into these dew drops. Loss of small organic compounds might affect results of the optical properties of secondary organic aerosol. It should be described whether dew drops appeared during experiments or not.

(8) Line 18, page 5. What is AIM? Please explain this abbreviation.

(9) The first paragraph of section 3.1 and Fig. 1. Why did the NO concentration decreased much faster under a dry acidic condition than for other conditions?

(10) Lines 30 – 32, page 6. The authors describe “the optical properties of secondary organic aerosol should be concerned differently at different wavelength.” The meaning of this sentence is unclear. Please rewrite it.

(11) Line 38, page 6. Generally, “200 – 400 m/z” is written as “m/z 200 – 400.” According to IUPAC, m/z should be italic.

(12) Lines 15 – 16, page 7. The authors describe “oligomers above 500 Da appear high relative intensities.” Please show mass spectra obtained for experiments under dry and humid neutral conditions.

(13) Lines 1 – 2, page 8. How did the authors identify butanehexol, cyclohexanepentol,

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and methylpentitol? Experimental data shown for chemical identifications in this study are only mass spectra observed by direct sample infusion into the mass spectrometer. They could only suggest chemical formulae from observed mass spectra. The results of concentrations of alcohols are used as evidences for the formation of charge transfer complexes in this manuscript. The identifications of these alcohol products should be explained in detail.

(14) Lines 2 – 5, page 8. The gas-particle partitioning is determined by the aerosol mass concentration rather than the surface concentration (Pankow, 1994). The rate of reactive uptake due to surface reactions may be determined by the aerosol surface concentration.

(15) The second paragraph of section 3.4 and Figure 4. The authors describe only that Figures 4a and 4b are difference mass spectra between DS and WS. Please explain whether these figures show results of “DS – WS” or “WS – DS”? Similar explanations should be added for Figures 4c, 4d, S2a, and S2b. In addition, chemical formulae shown in these figures are too small. These should be enlarged.

(16) Lines 32 – 33, page 8. Which results show that the oligomer concentrations observed for WS experiments are higher than for DS? Both figures 4a and 4b show difference signals are very small for products with $m/z > 400$, suggesting that there was no big difference in the oligomer concentrations between WS and DS.

(17) Line 23, page 9. What is “complex pollution”? It should be explained specifically.

(18) Lines 1 – 2, page 10. The authors describe “a full climate model would be necessary to determine the actual forcing caused by this (these?) effects caused by SO₂ and humidity as well.” The meaning of this sentence is unclear. Please rewrite it.

(19) Lines 6 – 7, page 10. If the authors want to emphasize that the increase of the real part of refractive index, please discuss using real pert data only.

(20) Line 15, page 10. The authors specify “dehydration reactions” in the conclusions,

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but they did not discuss whether oligomerization process contains dehydration or not in the main text.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2019-540>, 2019.

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