Response to the comments of Reviewer #2

This work by Li et al. describes measurements of optical properties in relation with chemical composition of n-dodecane SOA under low-NO$_x$ and two different temperatures (5 ℃ and 25 ℃). The authors found that under low temperature, the real part of the refractive index (RI) at 375 nm and 532 nm is enhanced, corresponding to substantial oligomer formation. The authors hence conclude that the enhanced oligomer formation under low temperature lead to the higher RI. The results could be relevant to low visibility in urban areas during wintertime. Overall, the manuscript is well written and demonstrates new findings regarding SOA optical properties vs. chemical compositions. But a few major concerns need to be addressed before this manuscript can be considered publishing.

Response: We thank Anonymous Referee #2 for the review and the positive evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

Specific comments:

1. Line 49 – 52. Although it is true that few studies have examined temperature effects on RI values of SOA, temperature effect studies on SOA formation and composition are not limited. There are many other studies on SOA formation and temperature effects not cited. For example, Warren et al., 2009, 43, 3548, Atmos. Environ.; Emanuelsson et al., 2013, 117, 10346, J. Phys. Chem. A.; Price et al., 2016, 50, 1216, Aerosol. Sci. Technol.; Boyd et al., 2017, 51, 7831, Environ. Sci. Technol.; Zhao et al., 2019, 3, 2549, ACS Earth Space Chem., etc.

We have revised this part in the manuscript, and the references mentioned above have been cited:

"There are also many studies investigating temperature effects on SOA formation and composition (Takekawa et al., 2003; Svendby et al., 2008; Clark et al., 2016;

Lamkaddam et al., 2016; Huang et al., 2017; Qing Mu and Gerhard Lammel, 2018; Zhao et al., 2019; Boyd et al., 2017; Price et al., 2016; Emanuelsson et al., 2013; Qi et al., 2010; Warren et al., 2009); however, works on the effect of temperature on the SOA RI are limited (Kim et al., 2014)." (Page 2, Line 52-56)

References:

Boyd, C. M., Nah, T., Xu, L., Berkemeier, T., and Ng, N. L.: Secondary organic aerosol (SOA) from nitrate radical oxidation of monoterpenes: Effects of temperature, dilution, and humidity on aerosol formation, mixing, and evaporation, Environ. Sci. Technol., 51, 7831-7841, 10.1021/acs.est.7b01460, 2017.

Emanuelsson, E. U., Watne, A. K., Lutz, A., Ljungstrom, E., and Hallquist, M.: Influence of humidity, temperature, and radicals on the formation and thermal properties of secondary organic aerosol (SOA) from ozonolysis of beta-pinene, J. Phys. Chem. A, 117, 10346-10358, 10.1021/jp4010218, 2013.

Huang, W., Saathoff, H., Pajunoja, A., Shen, X., Naumann, K.-H., Wagner, R., Virtanen, A., Leisner, T., and Mohr, C.: α-Pinene secondary organic aerosol at low temperature: Chemical composition and implications for particle viscosity, Atmos. Chem. Phys., 18, 2883-2898, https://doi.org/10.5194/acp-18-2883-2018, 2018.

Kim, H., Liu, S., Russell, L. M., and Paulson, S. E.: Dependence of real refractive indices on O:C, H:C and mass fragments of secondary organic aerosol generated from ozonolysis and photooxidation of limonene and alpha-pinene, Aerosol Sci. Technol., 48, 498-507, 10.1080/02786826.2014.893278, 2014.

Lamkaddam, H., Gratien, A., Pangui, E., Cazaunau, M., Picquet-Varrault, B., and Doussin, J.-F.: High-NOx photooxidation of n-dodecane: Temperature dependence of SOA formation, Environ. Sci. Technol., 10.1021/acs.est.6b03821, 2016.

Price, D. J., Kacarab, M., Cocker, D. R., Purvis-Roberts, K. L., and Silva, P. J.: Effects of temperature on the formation of secondary organic aerosol from amine precursors, Aerosol Sci. Technol., 50, 1216-1226, 10.1080/02786826.2016.1236182, 2016.

Qi, L., Nakao, S., Tang, P., and R., C. I. D.: Temperature effect on physical and chemical properties of secondary organic aerosol from m-xylene photooxidation, Atmos. Chem. Phys., 10, 3847-3854, 2010.

Qing Mu, M. S., Mega Octaviani, Nan Ma, Aijun Ding, Hang Su,, and Gerhard Lammel, U. P., Yafang Cheng: Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and transport of PAHs, Sci. Adv., 4, 10.1126/sciadv.aap7314, 2018.

Svendby, T. M., Lazaridis, M., and Tørseth, K.: Temperature dependent secondary organic aerosol formation from terpenes and aromatics, J. Atmos. Chem., 59, 25-46, 10.1007/s10874-007-9093-7, 2008.

Takekawa, H., Minoura, H., and Yamazaki, S.: Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, Atmos. Environ., 37, 3413-3424, 10.1016/s1352-2310(03)00359-5, 2003.

Warren, B., Austin, R. L., and Cocker, D. R.: Temperature dependence of secondary organic aerosol,

Atmos. Environ., 43, 3548-3555, 10.1016/j.atmosenv.2009.04.011, 2009.

Zhao, Z., Le, C., Xu, Q., Peng, W., Jiang, H., Lin, Y.-H., Cocker, D. R., and Zhang, H.: Compositional evolution of secondary organic aerosol as temperature and relative humidity cycle in atmospherically relevant ranges, ACS Earth Space Chem., 3, 2549-2558, 10.1021/acsearthspacechem.9b00232, 2019.

2. Line 78. Although details of the chamber can be referred to previous work, important and fundamental characteristics of the chamber still needs to be provided. For example, the material and volume of the chamber.

We have added the important and fundamental characteristics of the chamber in the **2.1 Smog Chamber Experiments** part:

"The chamber consisted of two 5 m^3 reactors made of fluorinated ethylene propylene (FEP) Teflon-film, which were housed in a thermally isolated enclosure. The temperature in the chamber was accurately controlled by high-power air conditioner in the range of -10 - 40 °C." (Page 3, Line 82-84)

3. Some important details of the chamber experiments are missing. Why were instruments not connected before temperature was stabilized? SOA mass concentration in each experiment should be reported (in Table 1 or in the main text). How long were filter samples collected and at what flow rate? After the filters were dissolved in filter, were the solutions sonicated? If not, how good were the extraction recoveries?

Actually, the instruments were connected at room temperature condition, when the temperature dropped to 5 ℃ and stabilized, the data measured by the instruments would to counted as valid data. And we have added this explanation in the main text (Page 3, Line 97-99).

We have added SOA mass concentration in Table 1 (Page 17, Line 605):

Table 1. The initial conditions of the smog-chamber experiments.

Experiments No.[a]	HC (ppb)	H$_2$O$_2$ (ppm)	NO$_X$ (ppb)	RH (%)	Temperature (℃)	Mass[b] (μg/m^3)
Dod-R-1	58	1.03	<1	<5	25	155
Dod-R-2	52	1.03	<1	<5	25	135

Dod-L-1	43	1.07	<1	<5	5	128
Dod-L-2	50	1.09	<1	<5	5	133

Each filter sample was collected for 30 min at 10 L/min flow rate. Then the filters were put into 5 mL methanol (99.9%, Fisher Chemical) and sonicated for 30 min. We have added this part in the manuscript (Page 4, Line 119-120).

4. How did the extinction coefficient and extinction efficiency evolve over the course of an experiment?

With the progress of the reaction, the surface mean diameter of the particles gradually increased, and the extinction coefficient and extinction efficiency of the particles increased as well. We chose two sets of experiments under two temperature conditions as examples. The figure below has been added in the Supporting Information of the manuscript. (Supporting Information, Page 7, Figure S4.)
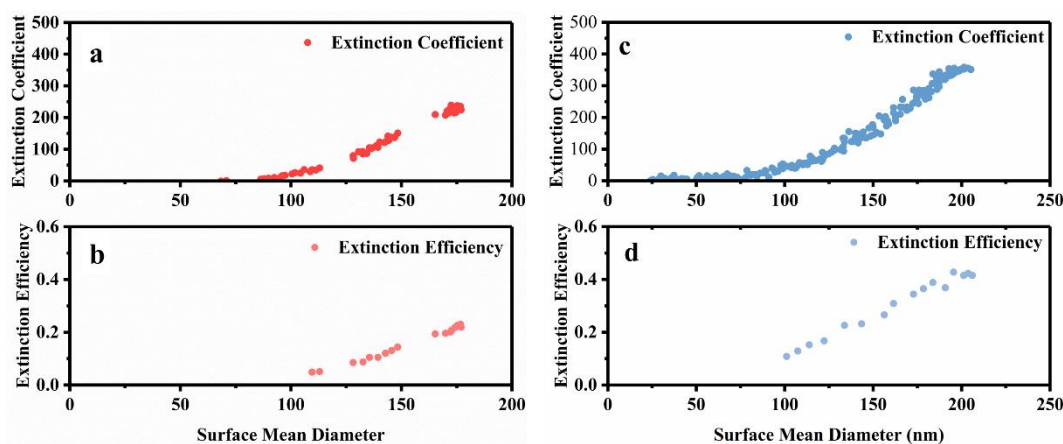

Figure S4. Evolution of optical parameters at 532 nm. Extinction coefficient (a) and efficiency (b) at room temperature; extinction coefficient (c) and efficiency (d) at low temperature.

5. Line 122. It is unclear how was the RI value uncertainty estimated from the various uncertainties. An equation needs to be provided.

We have added the estimating method and equations in the Supporting Information: (Supporting Information, Page 2, Line 28-43)

"The RI values are obtained with extinction efficiency (Q_{ext}) and surface mean

diameter (D_s). The uncertainty of the D_s measured by SMPS is $\pm\ 1\%$. The uncertainty of the extinction efficiency is calculated as the following:

The extinction efficiency can be expressed as:

$$Q_{ext} = \alpha_{ext} / (\frac{1}{4} N\pi D^2)$$

The three variables α_{ext}, N, D are independent and the uncertainty of them were 3%, 10% and 1%, respectively. Considering the propagation of uncertainty, we can obtain the variance formula:

$$\sigma_Q^2 = \sigma_\alpha^2 \left(\frac{\partial Q}{\partial \alpha}\right)^2 + \sigma_N^2 \left(\frac{\partial Q}{\partial N}\right)^2 + \sigma_D^2 \left(\frac{\partial Q}{\partial D}\right)^2$$

Then the uncertainty of Q_{ext} can be calculated as:

$$\frac{\sigma_Q}{Q} = \sqrt{\left(\frac{\sigma_\alpha}{\alpha}\right)^2 + \left(\frac{\sigma_N}{N}\right)^2 + 4\left(\frac{\sigma_D}{D}\right)^2} = \sqrt{0.03^2 + 0.1^2 + 4 \times 0.01^2}$$

$$= \sqrt{0.0113} = 10.6\%$$

The measured extinction efficiency ($Q_{ext,mea}$) is compared to calculated extinction efficiency ($Q_{ext,cal}$). The best-fit RI value is determined by minimizing the following reduced merit function (χ_r):

$$\chi_r = \frac{1}{N} \sum_{i=1}^{N} (Q_{ext,mea} - Q_{ext,cal}(n, k))_i^2$$

The uncertainty of the retrieval method is $\pm\ 0.002$, and the uncertainty of the measured extinction efficiency is $\pm\ 10.6\%$, resulting in the final uncertainty of the retrieved RI value to be about 0.02-0.03."

6. Line 123 – 124. The description of the RI prediction is not sufficient. A little more background should be provided. It appears molecular formulas are needed as input for the prediction. More details of the input are needed. Also, how the predictions will be used in this study were not mentioned.

We have added the following section to the main text (Page 6, Line 166-182):

"**2.3.2 Calculation Method of the QSPR Based on the Molecular Formula**

Using the molecular formula obtained from ESI-TOF-MS, we calculated the RI

values of the products in SOA with the quantitative structure–property relationship (QSPR) method (Redmond and Thompson, 2011). The QSPR can be expressed with Equation (9):

$$RI_{predicted} = 0.031717(\mu) + 0.0006087(\alpha) - 3.0227\left(\frac{\rho_m}{M}\right) + 1.38709 \quad (9)$$

where μ is the unsaturation of the molecular formula, α is the polarizability of the molecular formula, ρ_m is the mass density (g/cm^3), and M is the molar mass (g/mol).

The mass density of the compound is estimated by AIM model, the detailes of which can be referred to Girolami (1994).

μ is calculated through the conventional approach, which is used in many organic chemistry texts, Equation (10)

$$\mu = (\#C + 1) - 0.5(\#H - \#N) \quad (10)$$

where #C,#H, and #N are the number of the C, H, and N respectively.

α is calculated based on the molecular formula of the compound, it can be expressed by Equation (11):

$$\alpha = 1.51(\#C) + 0.17(\#H) + 0.57(\#O) + 1.05(\#N) + 2.99(\#S) + 2.48(\#P) +$$
$$0.22(\#F) + 2.16(\#Cl) + 3.29(\#Br) + 5.45(\#I) + 0.32 \quad (11)$$

where # is the number of the atoms of each element in the molecular formula.

The calculated RI values of products were used to link chemical composition and optical properties, and to explain the obseved RI differences at different temperatures in Sect. 3.4."

Reference:

Redmond, H., and Thompson, J. E.: Evaluation of a quantitative structure-property relationship (QSPR) for predicting mid-visible refractive index of secondary organic aerosol (SOA), Phys. Chem. Chem. Phys. : PCCP, 13, 6872-6882, 10.1039/c0cp02270e, 2011.
Girolami, G. S.: A simple" back of the envelope" method for estimating the densities and molecular volumes of liquids and solids, J. Chem. Edu., 71, 11, 962, 1994.

7. Line 150. In prior description (Line 122), the authors claimed that the uncertainty for RI values are 0.02 – 0.03. Here, the authors argue that change by 0.02 – 0.03 is a "substantial enhance effect" between the two temperatures, despite this change is on par with the uncertainty. A better case needs to be demonstrated regarding the enhancement of RI values at low temperature. In particular, this argument is a main result in this work.

In order to more intuitively display the RI variation tendency of SOA generated under two temperature conditions, we have added Figure 2 in the main text. As shown in Figure 2, the RI under low temperature conditions is enhanced whether at 532 nm or 375 nm. The enhancement of RI values under low temperature condition is still valid with experiment uncertainty. We have changed "a substantial enhance effect" into "an enhance effect" in the revised manuscript. (Page 8, Line 219)
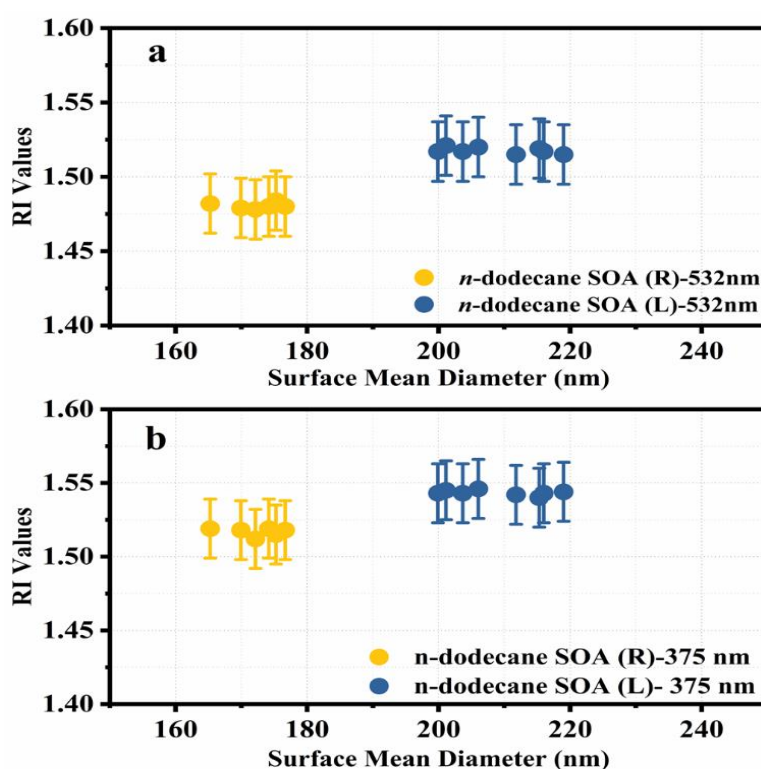

Figure 2. Variation tendency of the RI values as a function of surface mean diameter for SOA produced under room and low temperature conditions at (a) 532 nm and (b) 375 nm.

8. Section 3.3. and Figure 2. From the chemical composition measured by ESITOFMS, the authors claimed that the largely different mass spectra are observed under lower temperature, due to enhanced oligomerization. It is unclear, however, how the changed temperature affected the chemical mechanisms that lead to different products. The discussion of higher oligomer formation under low temperature might be reasonable. But the difference in the monomer range does not make sense. The monomer products should be from the various RO$_2$ chemistry regardless of the temperature. They should

follow the same pattern. But in Figure 2, the monomer range in the two mass spectra show very different results. I wonder if the mass spectra shown here are reproducible? Two experiments were carried out for each condition. Do they show consistent mass spectra? Clark et al (2016, 50, 5564, Environ. Sci. Technol.) showed isoprene SOA ESI-TOFMS mass spectra under different temperatures. Similar to this work here, very different results were observed in the oligomer range, but not necessarily for monomers. Better clear discussions are need here, rather than speculations.

We have updated Figure 2b (now is Figure 3b) by removing impurity interferences at ~200 and 300 amu:
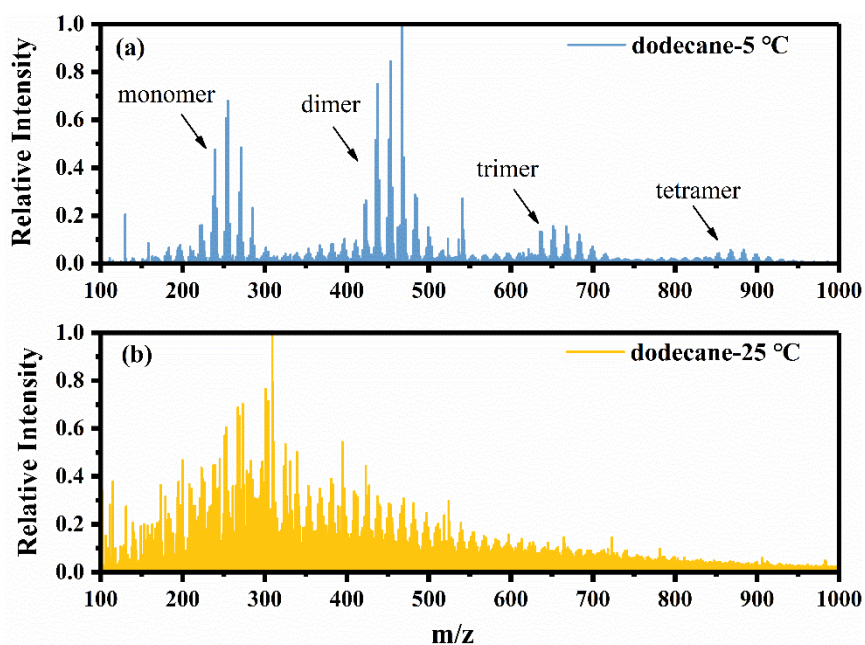

Figure 3. Mass spectra of *n*-dodecane SOA obtained by ESI-TOF-MS in positive ion mode. (a) low temperature condition; (b) room temperature condition.

The mass spectra under the same temperature condition are reproducible, see below the mass spectra of two experiments under room temperature. Though there are some slight differences in peak intensities, these two mass spectra are generally similar.
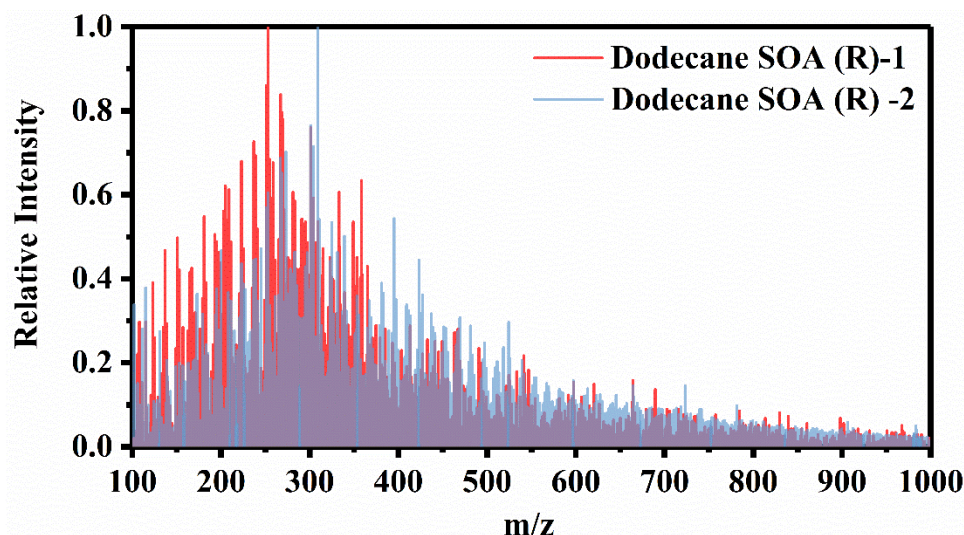
As the reviewer said, Clark et al. (2016) found that the SOA formed from isoprene had similar mass spectra at the monomer range at different temperatures. However, the precursors are very different (isoprene vs n-dodecane), which have very different oxidation pathways and partitioning processes. Hence, it is possible that we observe different results in mass spectra at monomer range.

As we have mentioned in the manuscript, the different oxidation degree and partitioning process have made the difference in monomer range. At room temperature, more OH oxidation steps in the gas phase can lead to the formation of some fragmentation products that may not be observed in the low temperature. For example, we have observed the high intensity of M/Z 195 $C_{10}H_{20}O_2$ (Relative Intensity 0.39), M/Z 211 $C_{10}H_{20}O_3$ (Relative Intensity 0.13) at room temperature but very low intensity (0.012, 0.041, respectively) at low temperature, and M/Z 195 and 211 are likely products from gas-phase OH oxidation. This process may be different from isoprene (Clark et al., 2016), because for n-dodecane the carbon number is high and volatility is low and fewer oxidation steps are needed before partitioning, while for isoprene there is only 5 carbon atoms so more oxidation steps are needed before partitioning no matter at room or low temperature.

Overall, the differences in monomer range still make sense.

We have added related statement in the main text. (Page 9, Line 262-273)

Reference:

Clark, C. H., Kacarab, M., Nakao, S., Asa-Awuku, A., Sato, K., and Cocker, D. R., 3rd: Temperature effects on secondary organic aerosol (SOA) from the dark ozonolysis and photo-oxidation of isoprene, Environmental Science & Technology, 10.1021/acs.est.5b05524, 2016.

9. Section 3.4. It appears to me that the validation of the authors' argument using calculation method is important to extend further. Since it is a short manuscript, I suggest the authors include the results based on the prediction in the main text.

Thanks for this suggestion. We have moved the calculation method to the main text, and they are highlighted in yellow in the "2.3 Calculation Method of RI Values" Section. (Page 4-6, Line 125-189). Figure S3, Figure S5, and Table S2 are also moved to the main text, and they have updated as Figure 4, Figure 6, and Table 2.

Technical comments:

1. Line 29. Change "heavy" to "heavily".

Page 1, Line 32: This has been corrected.

2. Line 62 – 68. When referring to prior temperature effect studies, it would be helpful to mention at what temperatures were those results observed.

Page 2, Line 67: The temperature ranges have been added.

3. In Figure 4, the y-axis between a and c, as well as b and d, are different. I suggestthe authors use the same y-aixs ranges for easier comparison.

Thanks for this suggestion. This has been corrected, and Figure 4 has been updated as Figure 7 in the main text.