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Thermal dissociation cavity-enhanced absorption spectrometer for measuring NO_2, RO_2NO_2, and $RONO_2$ in the atmosphere

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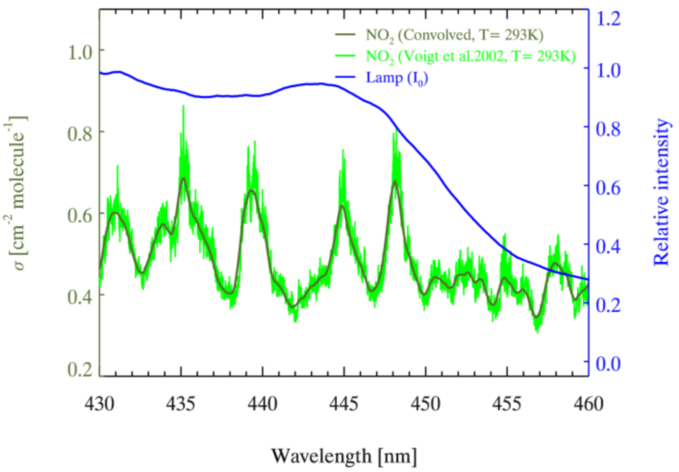

Figure S1. The cross section of NO_2 and the normalized intensity distribution of light source at 430-460 nm. Green line and dark green line are the absorption cross section before and after convolution. The blue line is the distribution of the relative light intensity when pure N_2 filled the optical cavity.

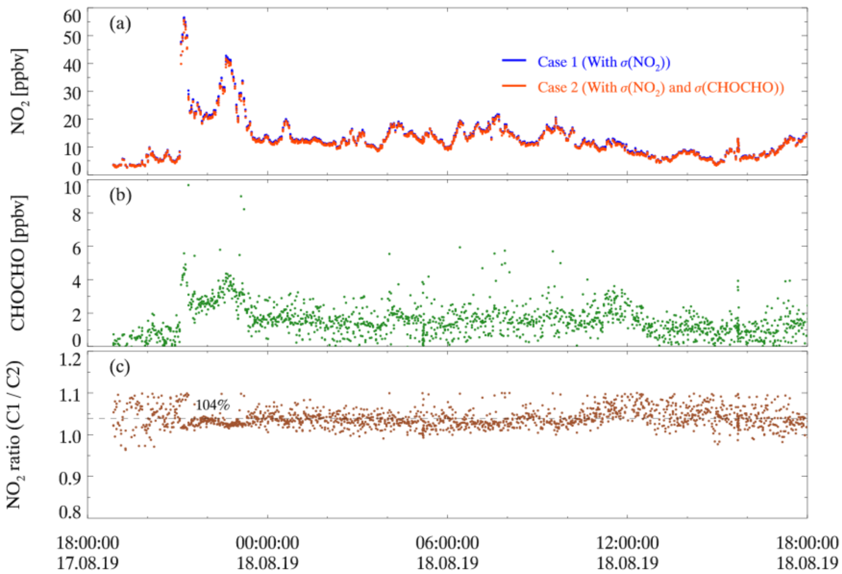

Figure S2. An example of the comparison about the fitting results with considering the cross section of glyoxal or without. Panels show the case on August 17, 2019 and August 18, 2019 during CHOOSE campaign. Panel (a) shows the time series of NO_2 under two different conditions. Panel (b) shows the time serie of glyoxal under Case 2. Panel (c) shows the concentration ratio of NO_2 under two different cases.

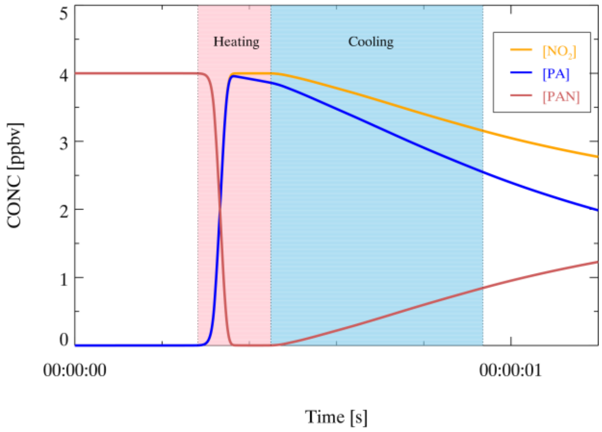

Figure S3. A simulated example of the PAN pyrolysis in the PNs channel at 180 °C if the PAN source is equal to 4 ppbv. The concentration of relative species changes with the residence time, the red line is concentration of PAN, the blue line is the concentration of PA radical, and the yellow line is the concentration of NO_2. The red part in the plot is the duration time when the air flow goes through the heating part of quartz tube, and the blue part is the duration time when the air flow goes through the cooling part.

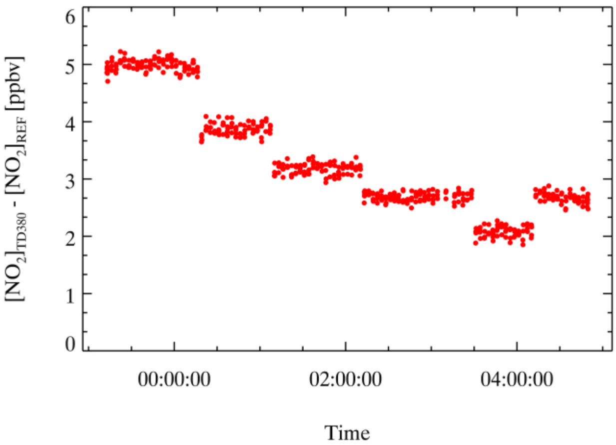

Figure S4. The raw time series of difference in NO_2 mixing ratio between the ANs channel and the reference channel when change the concentration of the PAN source. The measurements were done under the normal sampling and the time resolution is 6 seconds.

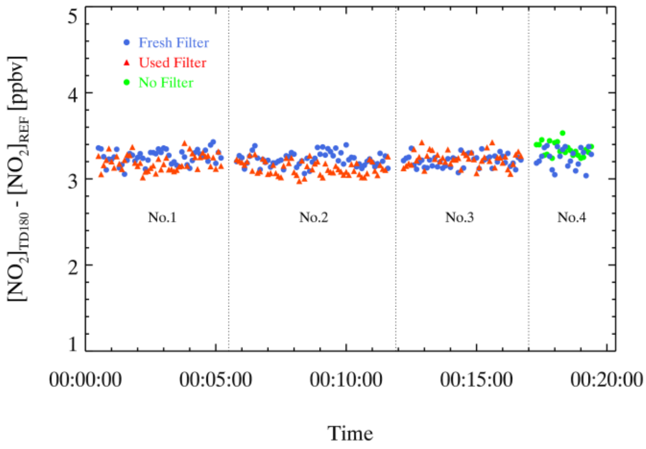

Figure S5. Measurements of difference in NO_2 mixing ratio between the PNs channel and the reference channel when putting the different filters in filter holder under normal sampling. The measurements are divided into 4 groups (NO.1 - 4). The first 3 groups (NO.1 - 3) are set to measure the difference between the fresh and the used conditions, and the last one is to measure the influence of filter use. Blue points represent the results when using the fresh filters and the green points represents the situation when no filters are used. The triangles represent the results when using the used filters.

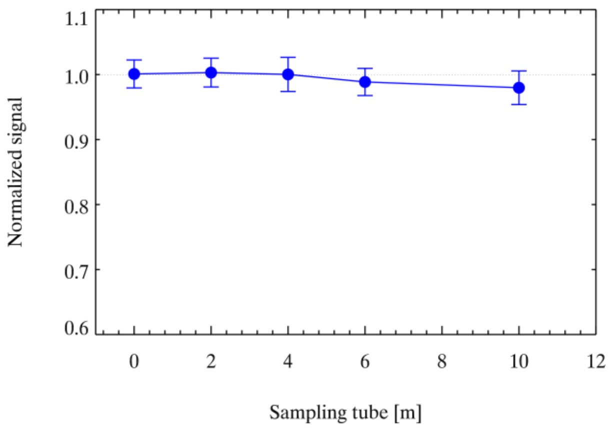

Figure S6. Measurements of the different signal of NO_2 mixing ratio in PNs channel when using the different length sampling tubes to measure the same PAN source. The normalized signal was calculated based on the signal of NO_2 mixing ratio when the lengthen of sampling tube equal to zero. The error bars represent one standard deviation.

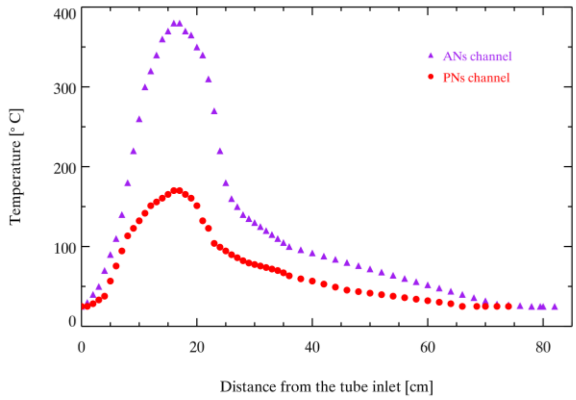

Figure S7. The temperature profiles of the heated channels. The temperature profile of the cooling line after the heated part (when the distance is greater than 25 cm) is measured by insertion of the thermocouple when the flowing rate is the same value during the sampling, and the heated part are simulated. Purple and red points are the temperature distribution from the inlet of quartz tube to the end of the channel in ANs channel and PNs channel, respectively.

Figure S8. The map of the observation site in Xinjin, Chengdu during CHOOSE campaign according to Baidu Maps. The red pentagram is the site location (Hubazi).

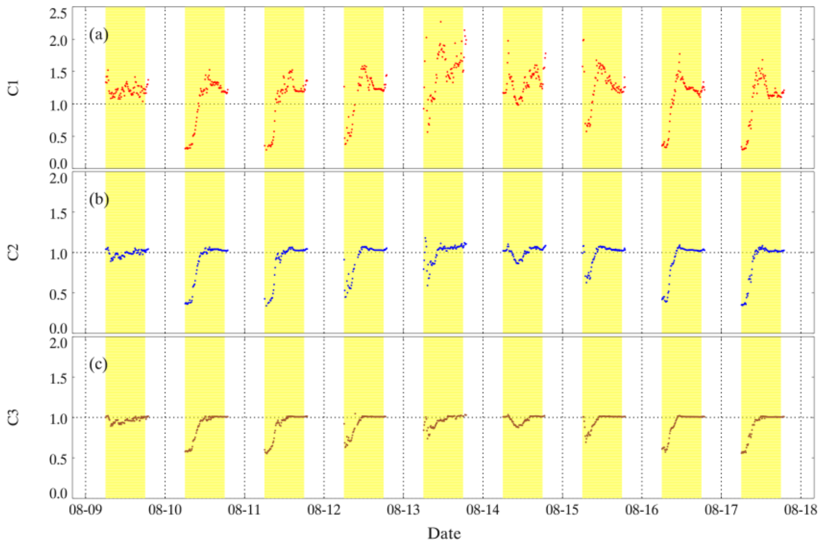

Figure S9. Time series of the correction factors for ONs measurements during the CHOOSE campaign as shown in Fig. 12. The yellow boxes indicate the period for the daytime. Panel (a) The red points represent the correction factors (*C1*) to correct the raw concentrations of PNs in PNs channel. Panel (b) The blue points represent the correction factors (*C2*) to get the raw concentrations of PNs in ANs channel. Panel (c) The brown points represent the correction factors (*C3*) to correct the raw concentrations of ANs in ANs channel.

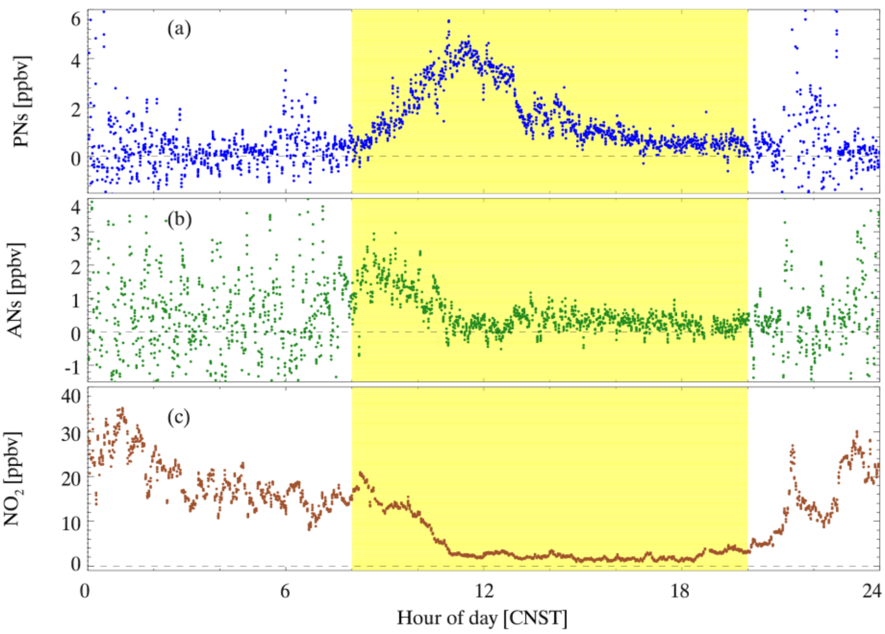

Figure S10. An example of the effect of sharp changes in NO_2 mixing ratio on the measurement of PNs and ANs. Panels show the case on August 15, 2019 during CHOOSE campaign. The yellow region indicates the time span for day-time. The blue, green, and brown points represent PNs mixing ratio, ANs mixing ratio, and NO_2 mixing ratio, respectively.

Text S1 List of the chemical mechanism of the box model

K1:	PAN-->CH3CO3+NO2
K2:	CH3CO3+NO2-->PAN
K3:	CH3CO3+NO-->NO2+CH3O2
K4:	CH3CO3+NO3-->NO2+CH3O2
K5:	CH3O2+NO-->0.001*CH3O2NO2+0.999*CH3O+0.999*NO2
K6:	CH3O2+NO2-->CH3O2NO2
K7:	CH3O2+NO3-->CH3O+NO2
K8:	CH3O2NO2-->CH3O2+NO2
K9:	HO2+NO-->HO+NO2
K10:	HO2+NO2-->HNO4
K11:	HNO4-->HO2+NO2
K12:	HO+NO2-->HNO3
K13:	HO+NO-->HONO
K14:	CH3CO3-->CH3CO
K15:	NO2+O3-->NO3
K16:	NO3+NO-->2*NO2
K17:	NO3+HO-->HO2+NO2
K18:	NO3+HO2-->0.7*HO+0.7*NO2+0.3*HNO3
K19:	NO3+NO2-->NO+NO2+O2
K20:	NO3+NO3-->2*NO2+O2
K21:	NO3+NO2-->N2O5
K22:	N2O5-->NO2+NO3
K23:	N2O5+H2O-->2*HNO3
K24:	CH3CO3+HO2 ->0.15*CH3CO2H+0.15*O3+ 0.41*CH3CO3H+0.44*CH3O2+0.44*HO
K25:	CH3O2+HO2-->CH3OOH
K26:	CH3O2+HO2-->HCHO
K27:	CH3OOH+HO-->0.6*CH3O2+0.4*HCHO
K28:	HO2+HO2-->H2O2+O2
K29:	HO2+HO2+H2O-->H2O2+H2O+O2
K30:	HO+HO2-->H2O+O2
K31:	CH3CO3H+HO-->CH3CO3
K32:	CH3NO3-->CH3O+NO2
K33:	CH3NO3+HO-->HCHO+NO2
K34:	CH3O-->HCHO+HO2
K35:	HO+HCHO-->HO2+CO
K36:	CH3CO+M-->CH3O2+M
K37:	CH3CO+O2+M-->CH3CO3+M
K38:	CH3CO+O2-->HO+CH2CO2
K39:	HO+CH3O2-->HO2+HO2
K40:	HO+CH3CO3-->HO2+CH3O2+CO2