

1 ***Support Information:***

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3 **Thermal dissociation cavity enhanced absorption spectrometer for**  
4 **detecting RO<sub>2</sub>NO<sub>2</sub> and RONO<sub>2</sub> in the atmosphere**

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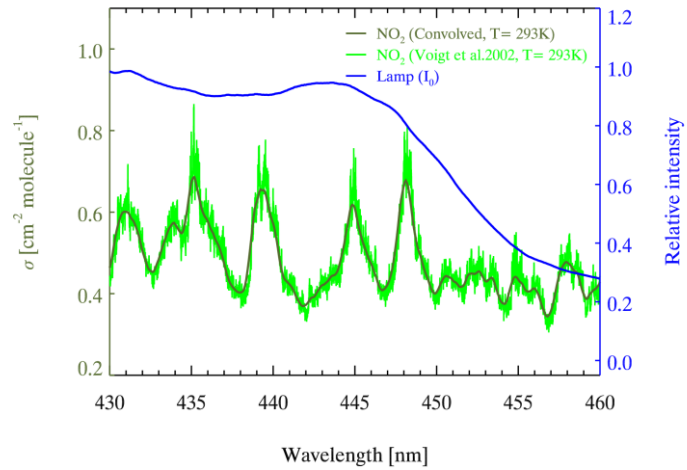
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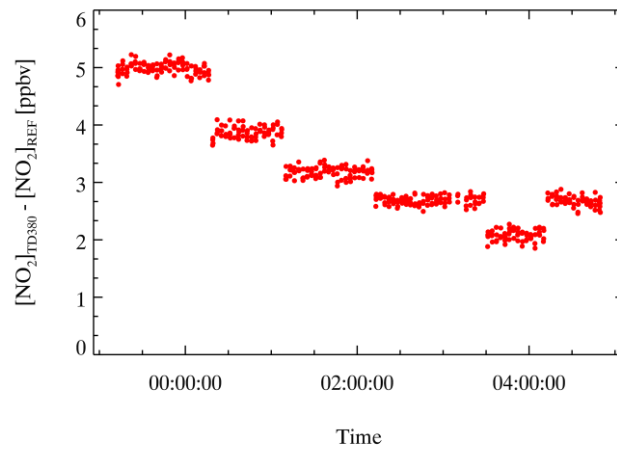
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17 Figure S1. The cross section of NO<sub>2</sub> and the normalized intensity distribution of light source at 430-460 nm. Green  
 18 line and dark green line are the absorption cross section before and after convolution. The blue line is the distribution  
 19 of the relative light intensity when pure N<sub>2</sub> filled the optical cavity.

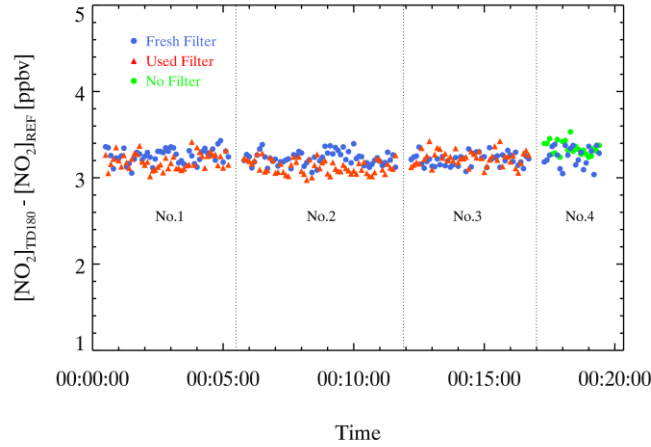
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22 Figure S2. The raw time series of difference in NO<sub>2</sub> mixing ratio between the ANs channel and the reference channel  
 23 when change the concentration of the PAN source. The measurements were done under the normal sampling and the  
 24 time resolution is 6 seconds.

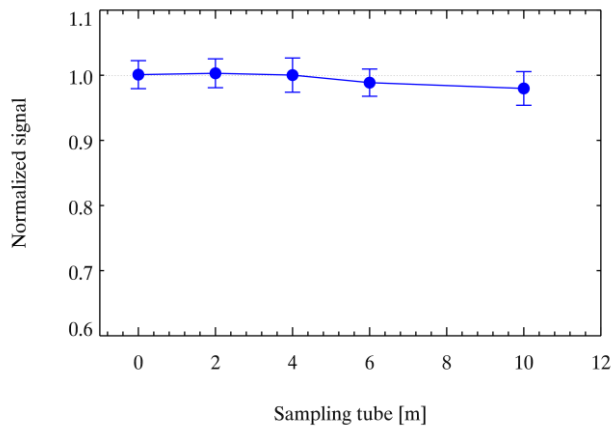
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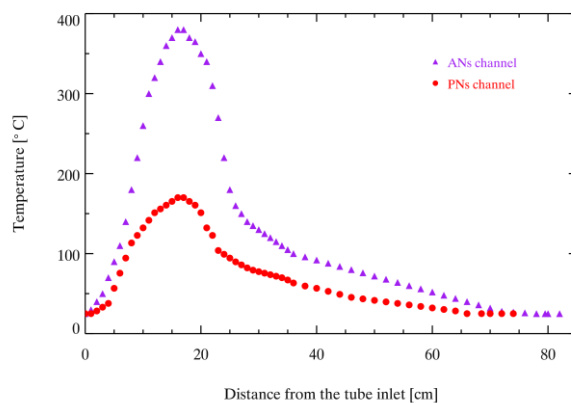
27 Figure S3. Measurements of difference in NO<sub>2</sub> mixing ratio between the PNs channel and the reference channel  
 28 when putting the different filters in filter holder under normal sampling. The measurements are divided into 4 groups  
 29 (NO.1 - 4). The first 3 groups (NO.1 - 3) are set to measure the difference between the fresh and the used conditions,  
 30 and the last one is to measure the influence of filter use. Blue points represent the results when using the fresh filters  
 31 and the green points represents the situation when no filters are used. The triangles represent the results when using  
 32 the used filters.

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35 Figure S4. Measurements of the different signal of NO<sub>2</sub> mixing ratio in PNs channel when using the different length  
 36 sampling tubes to measure the same PAN source. The normalized signal was calculated based on the signal of NO<sub>2</sub>  
 37 mixing ratio when the lengthen of sampling tube equal to zero. The error bars represent one standard deviation.  
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Figure S5. The simulated temperature profiles of the heated channels. 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.

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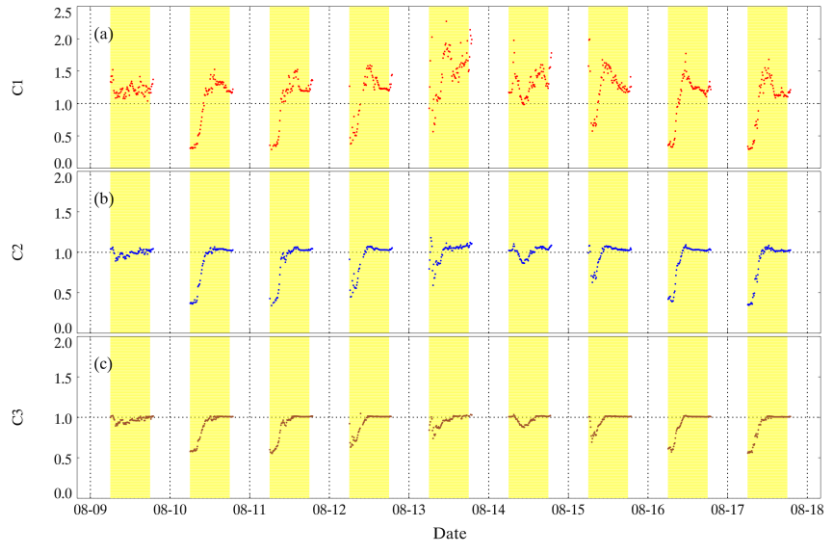
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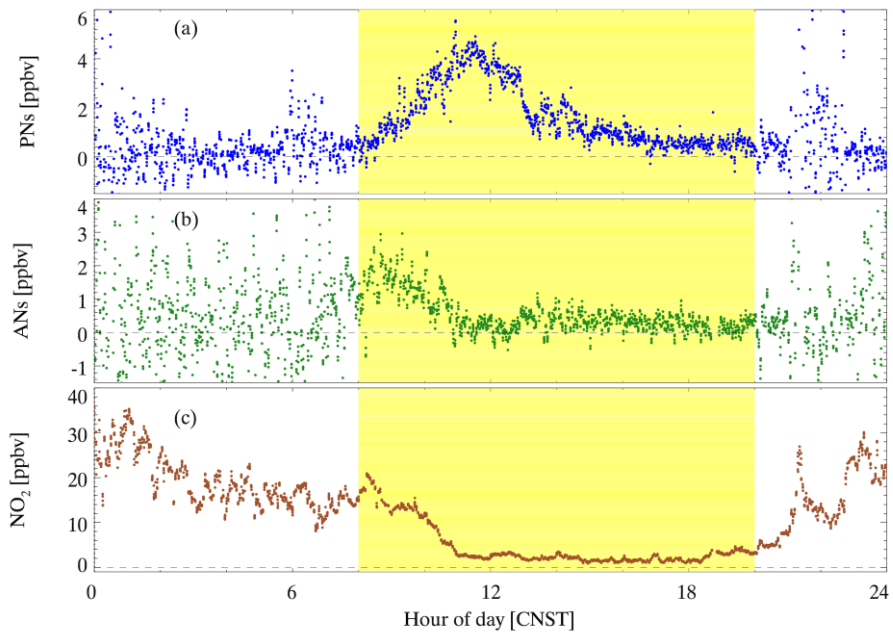
Figure S6. The map of the observation site in Xinjin, Chengdu during CHOOSE campaign according to Baidu Maps. The red pentagram is the site location (Hubazi).

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 49 Figure S7. Time series of the correction factors for ONs measurements during the CHOOSE campaign as shown in  
 50 Fig. 12. The yellow boxes indicate the period for the daytime. (a) the red points represent the correction factors (C1)  
 51 to correct the raw concentrations of PNs in PNs channel. (b) the blue points represent the correction factors (C2) to  
 52 get the raw concentrations of PNs in ANs channel. (c) the blue points represent the correction factors (C3) to correct  
 53 the raw concentrations of ANs in ANs channel.  
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 56 Figure S8. An example of the effect of sharp changes in  $\text{NO}_2$  mixing ratio on the measurement of PNs and ANs.  
 57 Panels show the case on August 15, 2019. The yellow region indicates the time span for day-time. The blue, green,  
 58 and brown points represent PNs mixing ratio, ANs mixing ratio, and  $\text{NO}_2$  mixing ratio, respectively.  
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61 **Text S1** List of the chemical mechanism of the box model

62 K1: PAN-->CH3CO3+NO2

63 K2: CH3CO3+NO2-->PAN

64 K3: CH3CO3+NO-->NO2+CH3O2

65 K4: CH3CO3+NO3-->NO2+CH3O2

66 K5: CH3O2+NO-->0.001\*CH3O2NO2+0.999\*CH3O+0.999\*NO2

67 K6: CH3O2+NO2-->CH3O2NO2

68 K7: CH3O2+NO3-->CH3O+NO2

69 K8: CH3O2NO2-->CH3O2+NO2

70 K9: HO2+NO-->HO+NO2

71 K10: HO2+NO2-->HNO4

72 K11: HNO4-->HO2+NO2

73 K12: HO+NO2-->HNO3

74 K13: HO+NO-->HONO

75 K14: CH3CO3-->CH3CO

76 K15: NO2+O3-->NO3

77 K16: NO3+NO-->2\*NO2

78 K17: NO3+HO-->HO2+NO2

79 K18: NO3+HO2-->0.7\*HO+0.7\*NO2+0.3\*HNO3

80 K19: NO3+NO2-->NO+NO2+O2

81 K20: NO3+NO3-->2\*NO2+O2

82 K21: NO3+NO2-->N2O5

83 K22: N2O5-->NO2+NO3

84 K23: N2O5+H2O-->2\*HNO3

85 K24: CH3CO3+HO2 ->0.15\*CH3CO2H+0.15\*O3+

86 0.41\*CH3CO3H+0.44\*CH3O2+0.44\*HO

87 K25: CH3O2+HO2-->CH3OOH

88 K26: CH3O2+HO2-->HCHO

89 K27: CH3OOH+HO-->0.6\*CH3O2+0.4\*HCHO

90 K28: HO2+HO2-->H2O2+O2

91 K29: HO2+HO2+H2O-->H2O2+H2O+O2

92 K30: HO+HO2-->H2O+O2

93 K31: CH3CO3H+HO-->CH3CO3

94 K32: CH3NO3-->CH3O+NO2

95 K33: CH3NO3+HO-->HCHO+NO2

96 K34: CH3O-->HCHO+HO2

97 K35: HO+HCHO-->HO2+CO

98 K36: CH3CO+M-->CH3O2+M

99 K37: CH3CO+O2+M-->CH3CO3+M

100 K38: CH3CO+O2-->HO+CH2CO2

101 K39: HO+CH3O2-->HO2+HO2

102 K40: HO+CH3CO3-->HO2+CH3O2+CO2