Supplementary information for "Online measurements of cycloalkanes based on NO^+ chemical ionization in proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS)"

Yubin Chen[1,2], Bin Yuan[1,2,*], Chaomin Wang[3], Sihang Wang[1,2], Xianjun He[1,2], Caihong Wu[1,2], Xin Song[1,2], Yibo Huangfu[1,2], Xiao-Bing Li[1,2], Yijia Liao[1,2], Min Shao[1,2]

[1] Institute for Environmental and Climate Research, Jinan University, Guangzhou 511443, China

[2] Guangdong-Hongkong-Macau Joint Laboratory of Collaborative Innovation for Environmental Quality, Guangzhou 511443, China

[3] School of Tourism and Culture, Guangdong Eco-engineering Polytechnic, Guangzhou 510520, China

Normalization the measurement data of NO+ PTR-ToF-MS

Here we normalize the raw data measured by NO^+ PTR-ToF-MS in the following way:

$$i[RH^+]_{norm} = \frac{i[RH^+]}{i[NO^+]} \times 10^6 \qquad (S1)$$

In this equation, $i[RH^+]_{norm}$ represents the signal value of normalized measurement data (ncps), $i[RH^+]$ represents the signal value of original measurement data (cps), nd $i[NO^+]$ represents the ion abundance of NO^+ ions. The $i[NO^+]$ is calculated from the ratio between ^{14}N and its isotopes ^{15}N, which is defined at 277 in this study.

Calculation method of instrument detection limit

The detection limit is the minimum concentration of the compounds that can be detected by the instrument and is related to the response factor, integration time, background signal and signal-to-noise ratio of the compounds to be tested. Assuming that both the statistical characteristic of the signal and the random error (noise) conform to the Poisson distribution, then according to the error transfer formula, the signal-to-noise atio can be expressed as:

$$\frac{S}{N} = \frac{C_f\ [X]\ t}{\sqrt{C_f [X]\ t + 2\ B\ t}} \qquad (S2)$$

where B represents the background signal, C_f is the calibration response factor, [X] represents the detection limit, and t is the integration time.The detection limit of cycloalkanes measured by NO^+ PTR-ToF-MS are calculated as the concentrations at which signal counts are 3 times the SD of measured background counts (Bertram et al., 2011; Wang et al., 2020; Yuan et al., 2017).

Table S1. Detailed information of the customized cylinder gas standard used in this study.

Standard Compound	Formula	CAS#	Concentration (ppb)	Uncertainty
Toluene	C_7H_8	108-88-3	101.7	±5%
Methacrolein	C_4H_6O	78-85-3	103.7	±5%
1,1,3,5-Tetramethylcyclohexane	$C_{10}H_{20}$	4306-65-4	100.5	±5%
Pentylcyclohexane	$C_{11}H_{22}$	4292-92-6	95.9	±5%
Hexylcyclohexane	$C_{12}H_{24}$	4292-75-5	96.0	±5%
Heptylcyclohexane	$C_{13}H_{26}$	5617-41-4	100.0	±5%
Octylcyclohexane	$C_{14}H_{28}$	1795-15-9	74.6	±5%
Octane	C_8H_{18}	111-65-9	100.8	±5%
Nonane	C_9H_{20}	111-84-2	100.1	±5%
Decane	$C_{10}H_{22}$	124-18-5	100.7	±5%
Undecane	$C_{11}H_{24}$	1120-21-4	97.4	±5%
Dodecane	$C_{12}H_{26}$	112-40-3	98.2	±5%
Tridecane	$C_{13}H_{28}$	629-50-5	99.4	±5%
Tetradecane	$C_{14}H_{30}$	629-59-4	96.0	±5%
Penadecane	$C_{15}H_{32}$	629-62-9	27.9	±5%

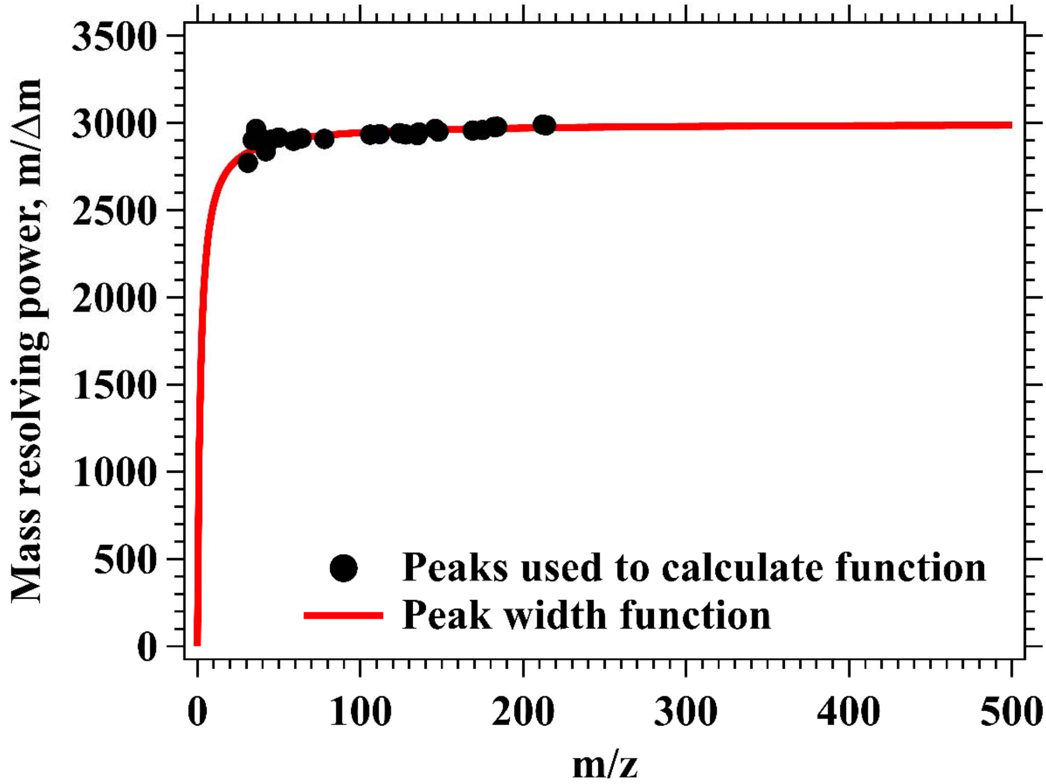

Figure S1. The relationship between mass resolving power and m/z.

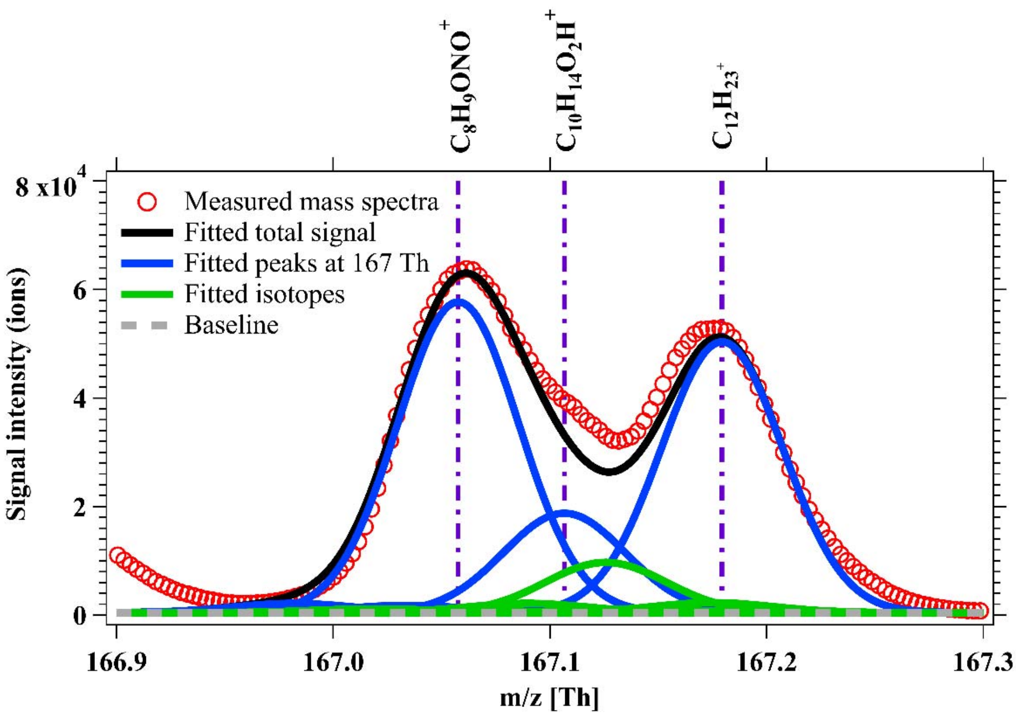

Figure S2. High-resolution peak fitting for *m/z* 167 to separate ion peaks of C_{12} cycloalkanes ($C_{12}H_{23}^+$) and other isomers ($C_8H_9ONO^+$ and $C_{10}H_{14}O_2H^+$) are detected using NO^+ PTR-ToF-MS.

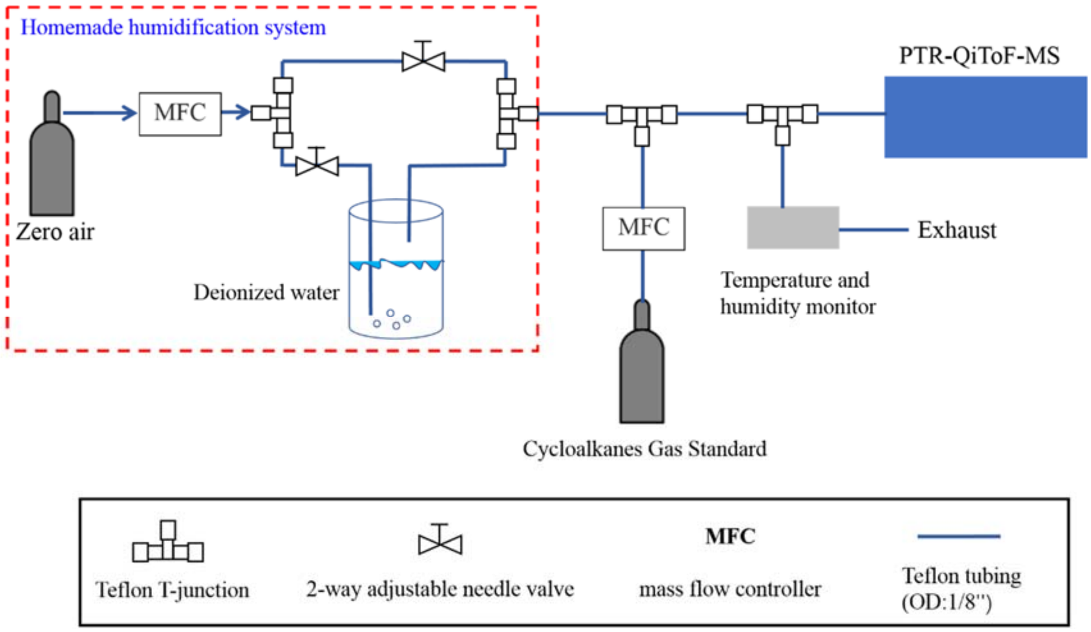

Figure S3. Schematic drawing of the custom-built humidity delivery system.

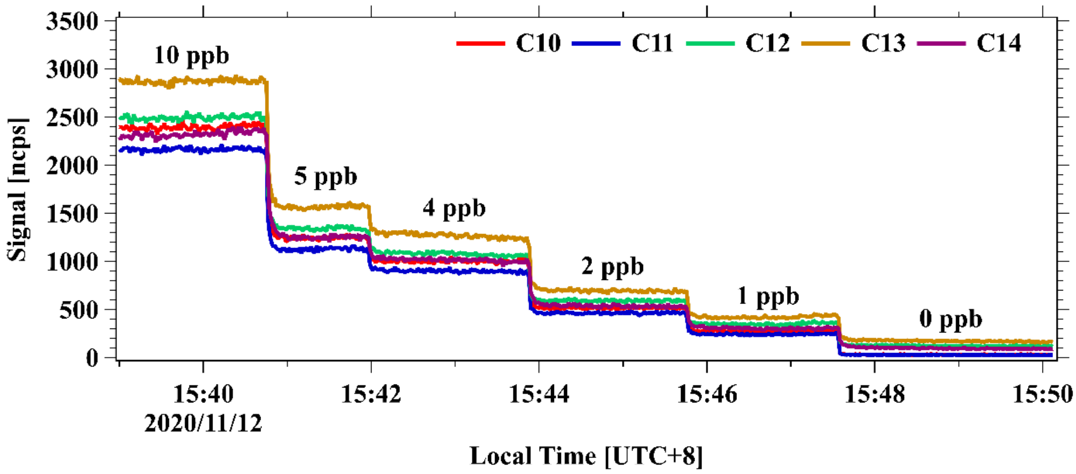

Figure S4. The multipoint calibrations of C_{10}-C_{14} cycloalkanes in dry condition (<1% RH).

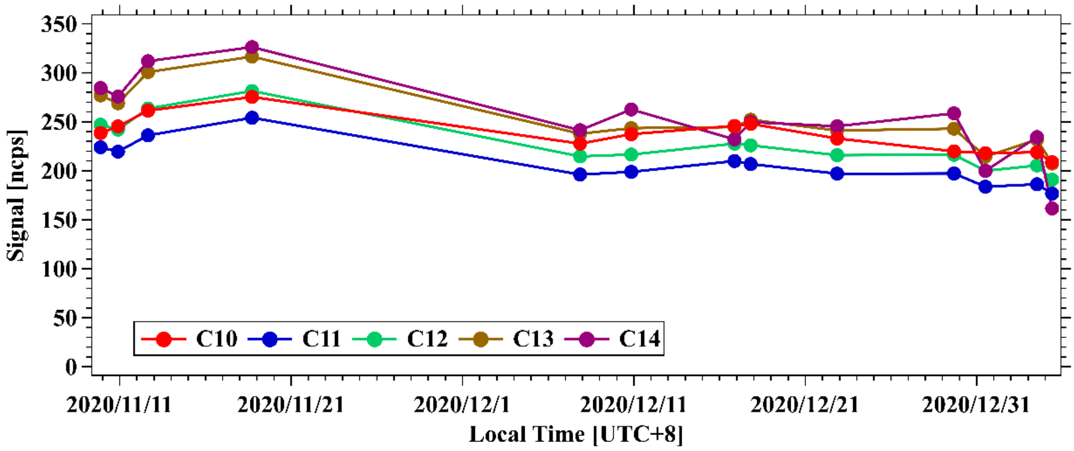

Figure S5. Calibration results of NO^+ PTR-ToF-MS for C_{10}-C_{14} cycloalkanes during the laboratory experiments.

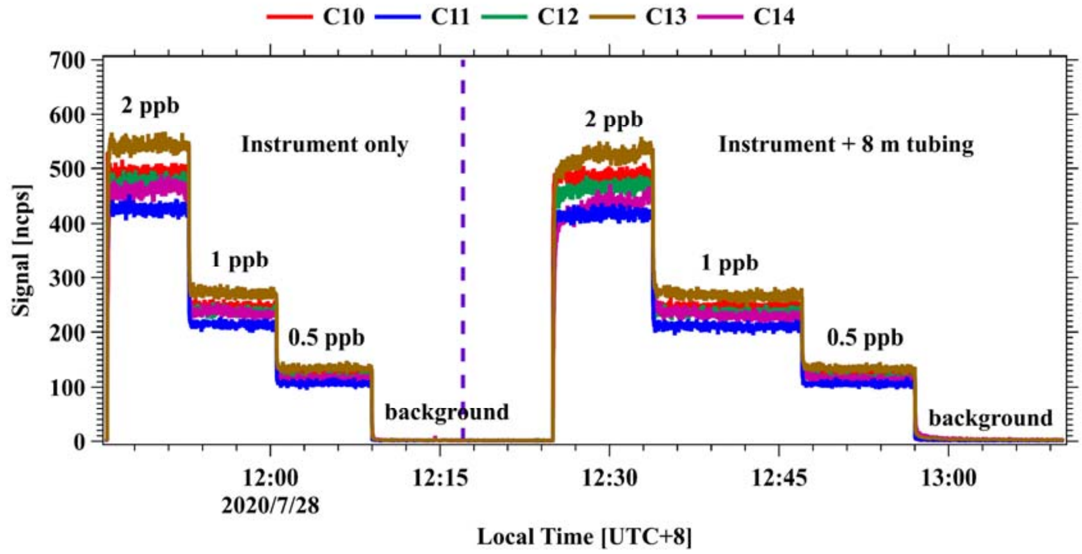

Figure S6. The tubing loss experiments of cycloalkanes (C_{10}-C_{14}) measured by NO^+ PTR-ToF-MS with an external pump at 5.0 L/min.

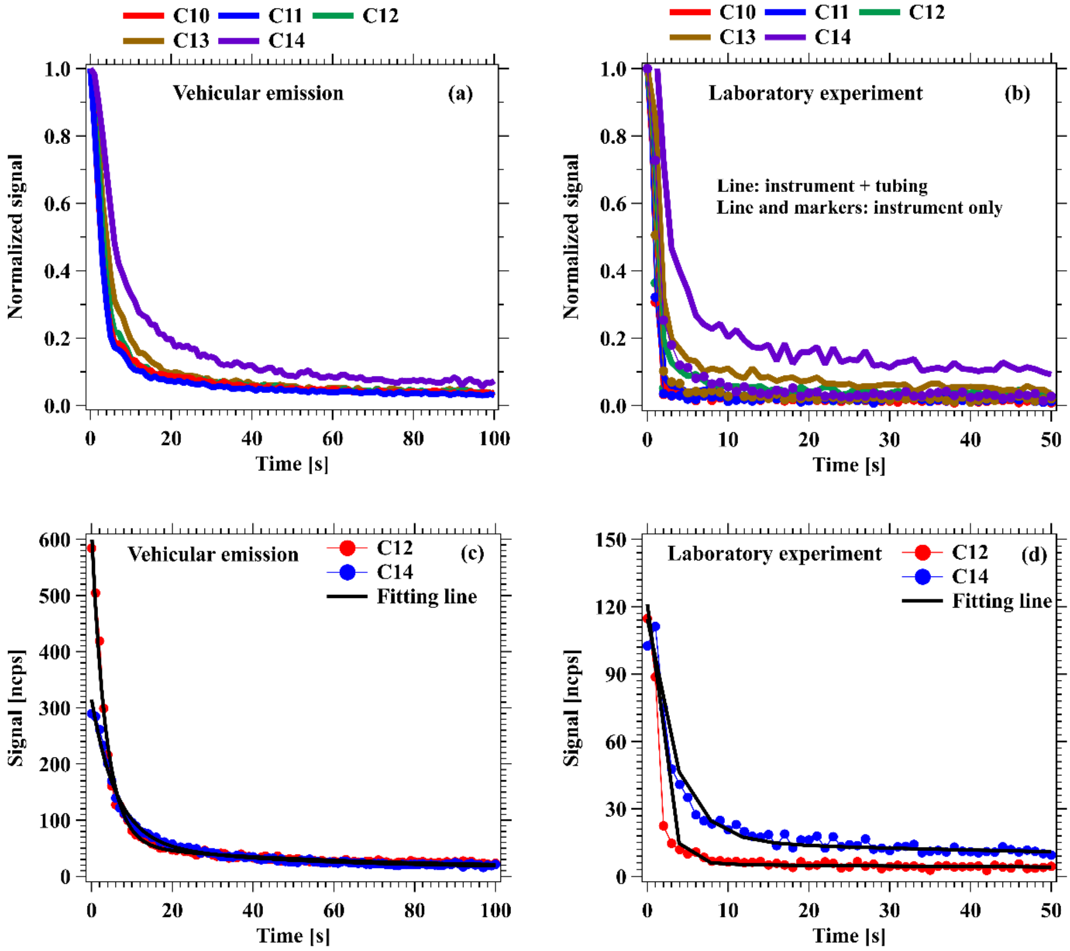

Figure S7. (a) The decrease in the normalized signal of cycloalkanes during the vehicular emission measurement. **(b)** The decrease in the normalized signal of cycloalkanes for instrument + tubing (line) and instrument only (line and markers) during the laboratory experiments. **(c-d)** The decrease in the signal of C_{12} and C_{14} cycloalkanes during the vehicular emission test and laboratory experiments, respectively. The data are fitted by a hyperbolic equation.

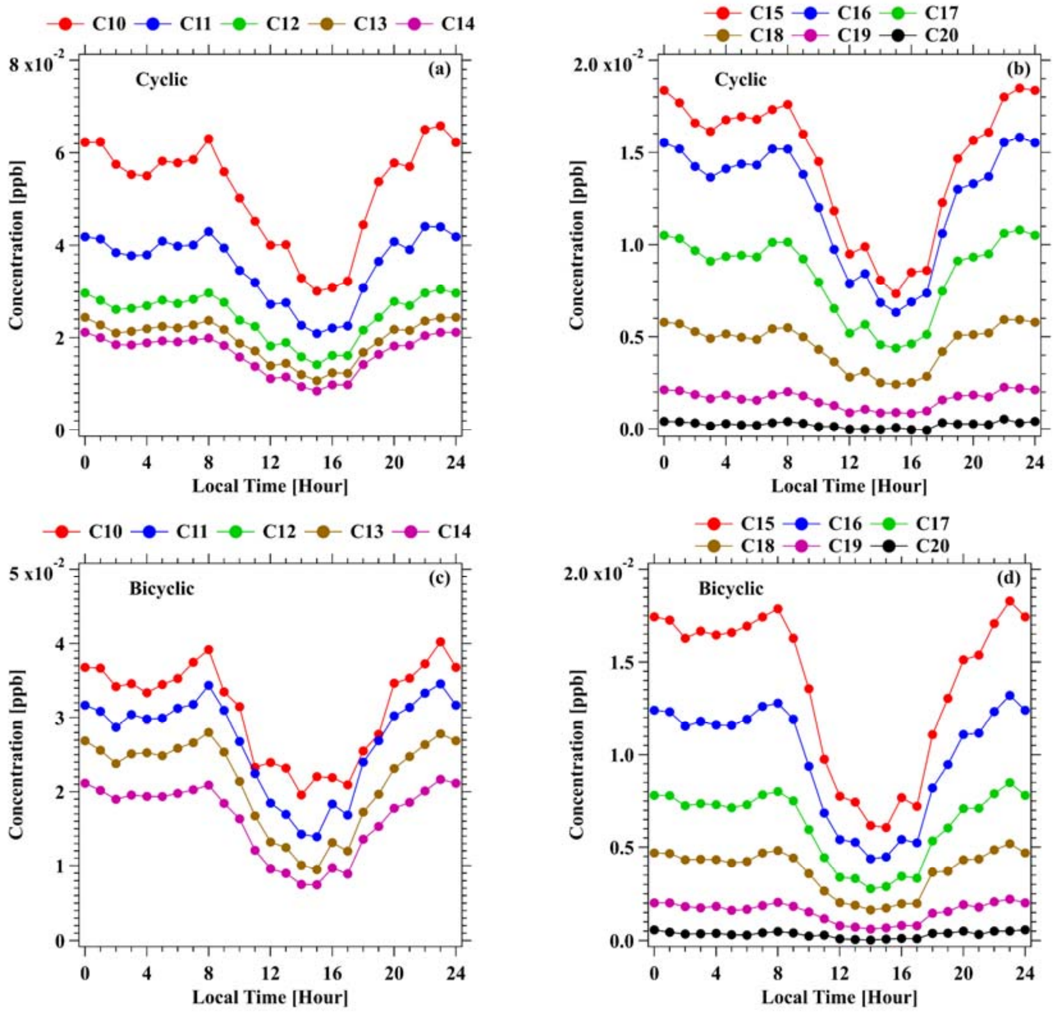

Figure S8. Diurnal variations of C_{10}-C_{20} cyclic and bicyclic alkanes during the campaign in urban region.

Reference

Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, Atmospheric Measurement Techniques, 4, 1471-1479, 2011.

Wang, C. M., Yuan, B., Wu, C. H., Wang, S. H., Qi, J. P., Wang, B. L., Wang, Z. L., Hu, W. W., Chen, W., Ye, C. S., Wang, W. J., Sun, Y. L., Wang, C., Huang, S., Song, W., Wang, X. M., Yang, S. X., Zhang, S. Y., Xu, W. Y., Ma, N., Zhang, Z. Y., Jiang, B., Su, H., Cheng, Y. F., Wang, X. M., and Shao, M.: Measurements of higher alkanes using NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmospheric Chemistry and Physics, 20, 14123-14138, 2020.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem Rev, 117, 13187-13229, 2017.