Supplement of

Characteristics and Formation of Negative Cluster Ions in an Urban Environment

Rujing Yin[1,2#], Xiaoxiao Li[1,3#], Chao Yan[2,3], Runlong Cai[2], Ying Zhou[3], Juha Kangasluoma[2], Nina Sarnela[2], Janne Lampilahti[2], Tuukka Petäjä[2], Veli-Matti Kerminen[2], Federico Bianchi[2], Markku Kulmala[2,3], Jingkun Jiang[1*]

[1]State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, China

[2]Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, 00014 Helsinki, Finland

[3]Aerosol and Haze Laboratory, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, 100029 Beijing, China

[#]These authors contributed equally to this work.

*: *Correspondence to*: J. Jiang (jiangjk@tsinghua.edu.cn)

This PDF file includes:

Page S1-S15
Figures S1 to S12
Tables S1

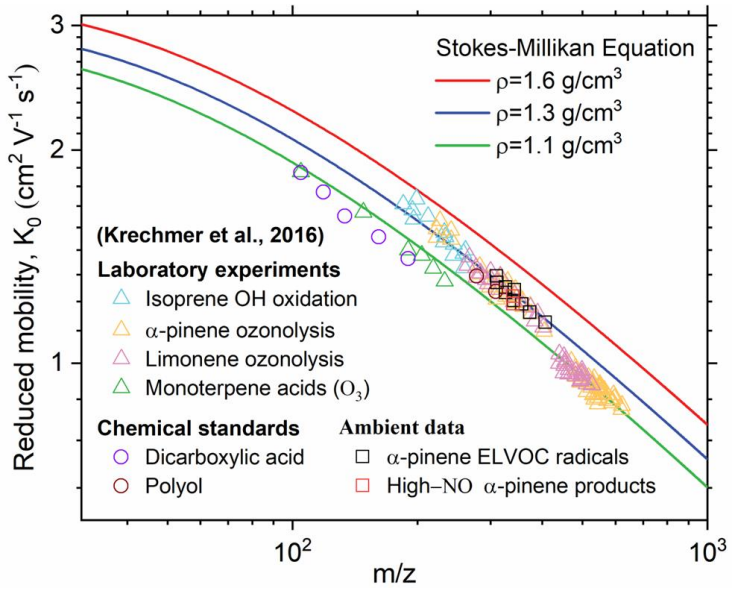


Figure S1. The measured reduced mobilities of different organic cluster ions in ion mobility spectrometer (Krechmer et al., 2016) and simulated mobilities based on the Stokes-Millikan equation using different densities.

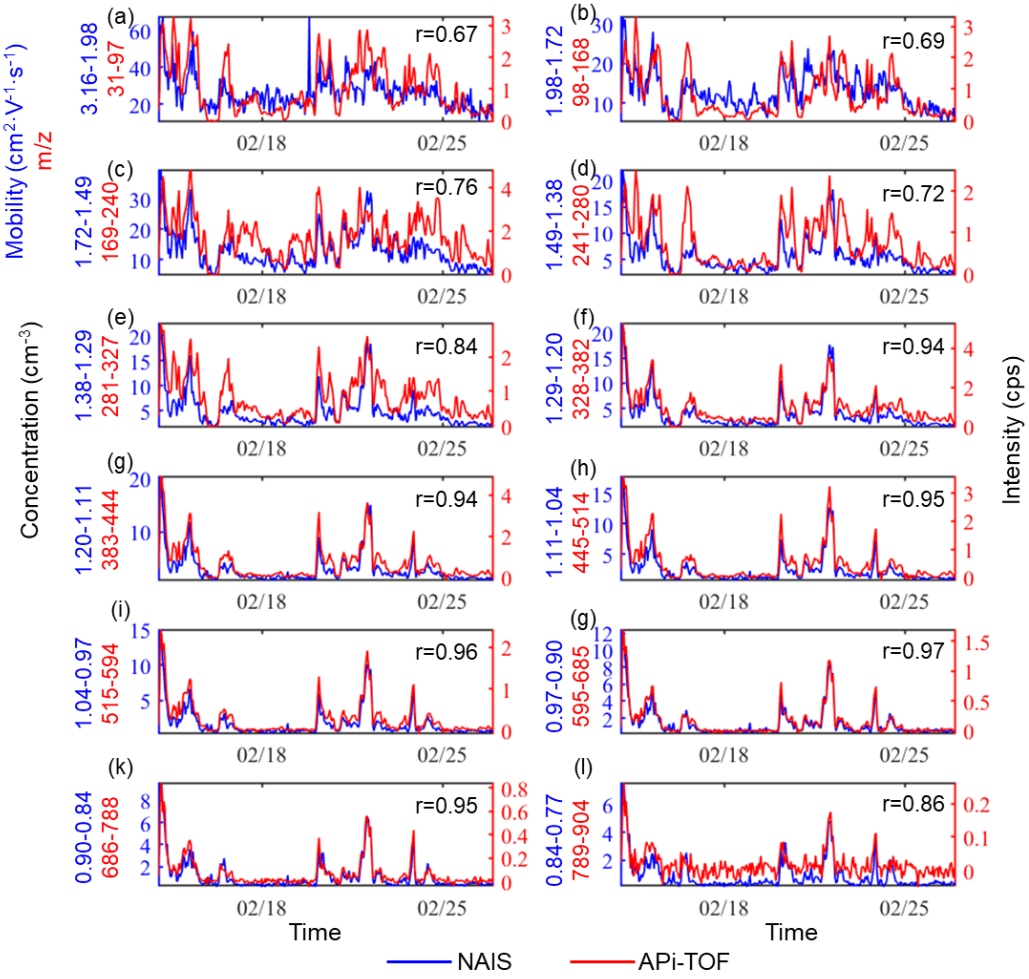


Figure S2. The concentrations of cluster ions with different mobility ranges measured by NAIS and the signal of cluster ions with corresponding m/z ranges measured by APi-TOF. The mobility and m/z is converted according to the method described in Section 2.2 in the main text.

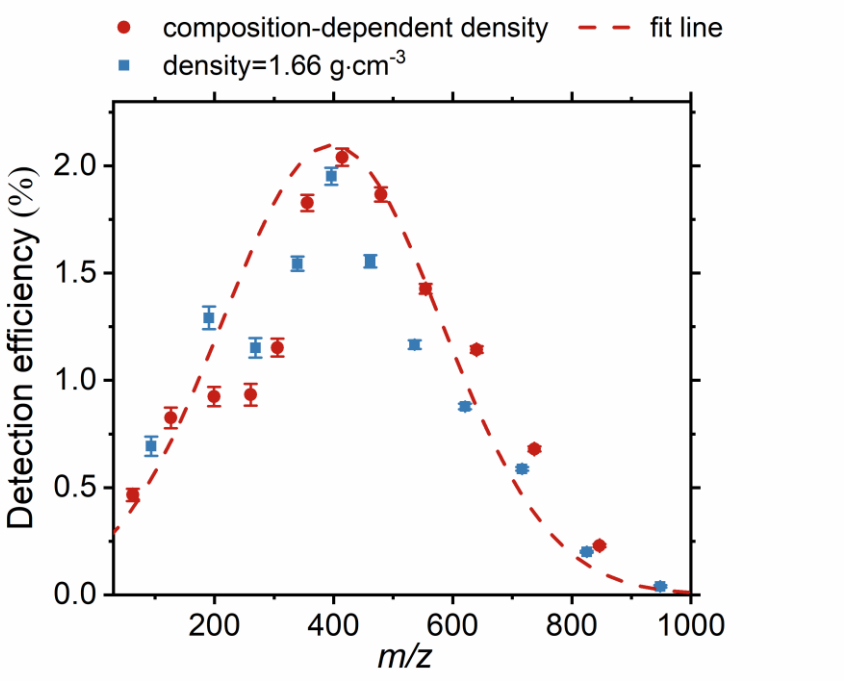


Figure S3. The concentrations of cluster ions with different mobility ranges measured by NAIS and the signal of cluster ions with corresponding m/z ranges measured by APi-TOF. The mobility and m/z is converted according to the method described in Section 2.2 in the main text.

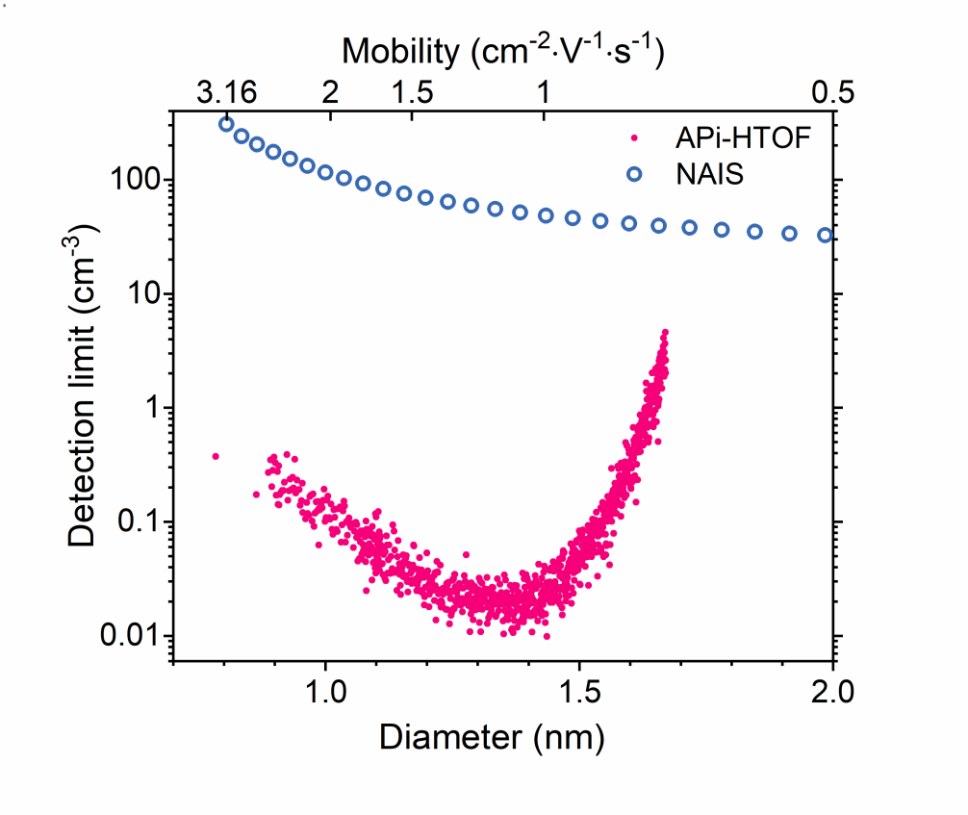
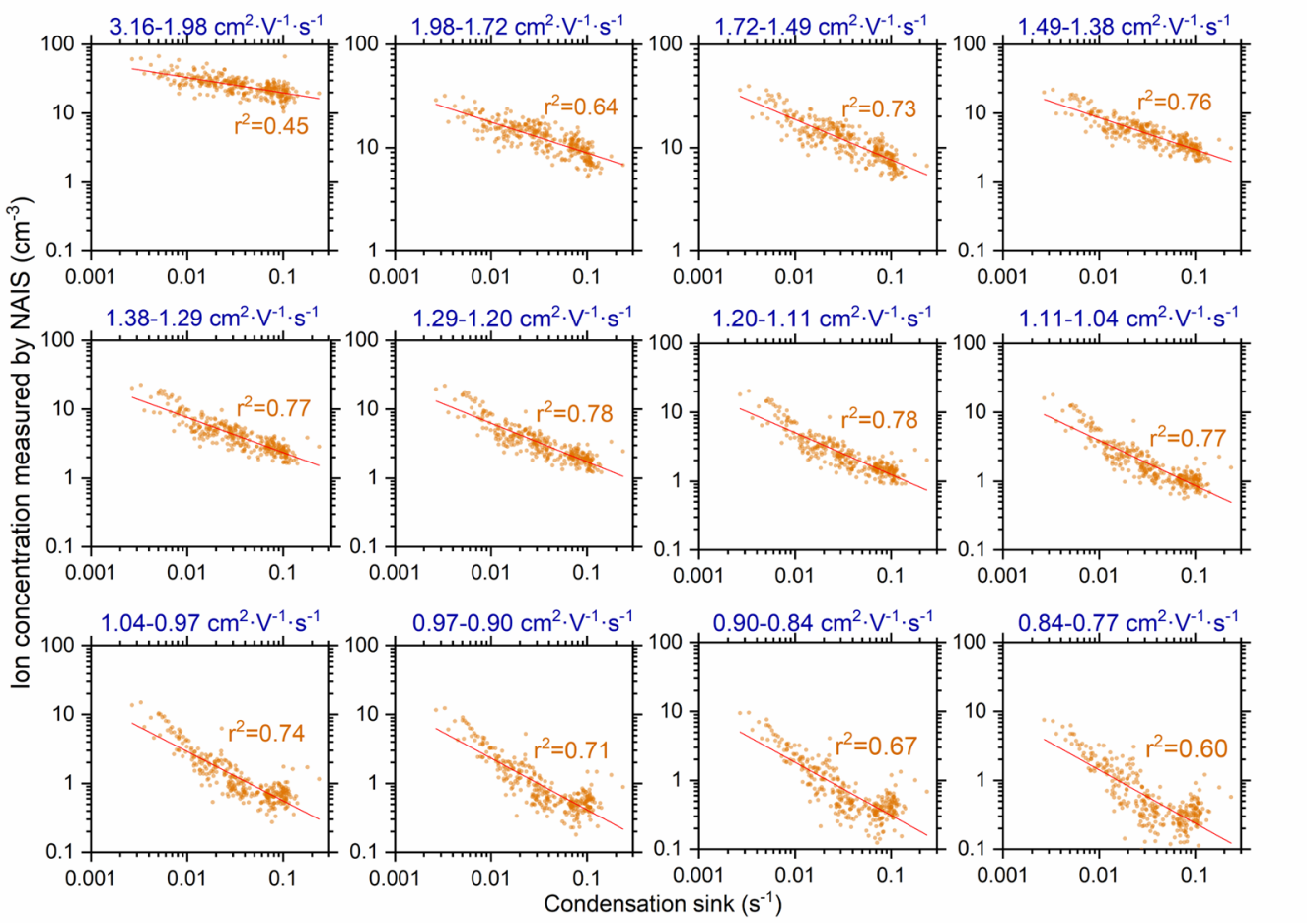


Figure S4. The concentrations of cluster ions with different mobility ranges measured by NAIS and the signal of cluster ions with corresponding m/z ranges measured by APi-TOF. The mobility and m/z are converted according to the method described in Section 2.2 in the main text.



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39 **Figure S5**. The scatter plots of CS and concentrations of cluster ions with different mobility ranges measured by NAIS in

40 urban Beijing, as well as the square of correlation coefficients.

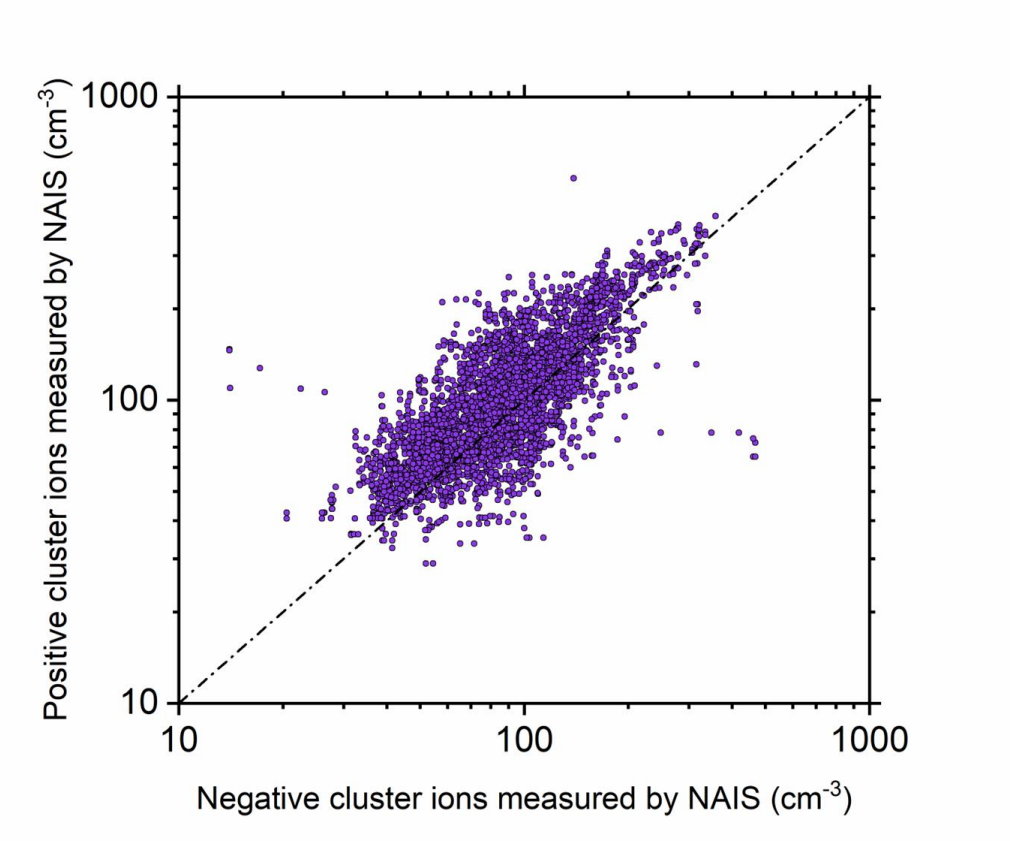
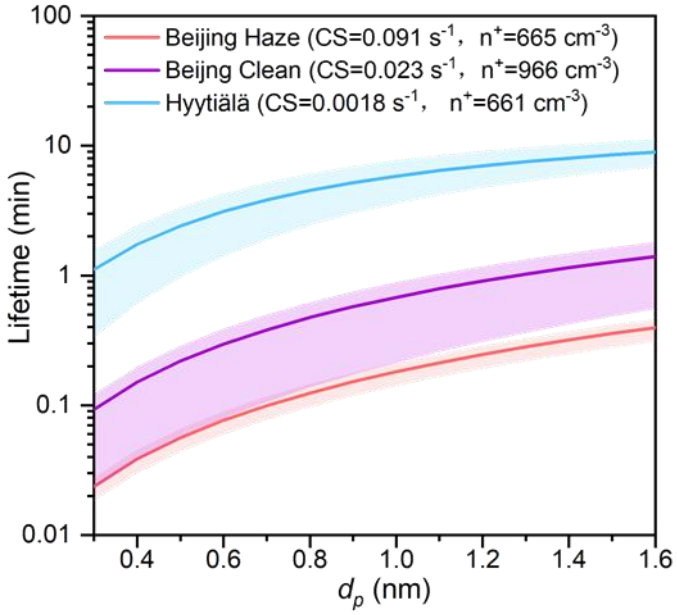


Figure S6. The scatter plots of the concentrations of negative and positive cluster ions measured by NAIS during the measurement in urban Beijing.



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46 **Figure S7**. The lifetime (the time needed for the concentration of a given ion concentration to decay to 1/e of its initial
47 value due to the coagulation loss to particles and recombination with opposite ions, calculated as $1/(CS \cdot dp^{-1.7}+\alpha n^{+})$) of
48 the cluster ions under typical conditions (i.e., the median value of CS and median of the total concentration of positive
49 ions in the range of 0.8-42 nm, n^{+}) during haze and clean periods in Beijing and Hyytiälä. The shadow regions represent
50 25-75% of the CS ranges, that is 0.074-0.11 s^{-1}, 0.013-0.034 s^{-1}, and 0.001-0.0023 s^{-1} during Beijing haze periods, Beijing
51 clean periods, and Hyytiälä.
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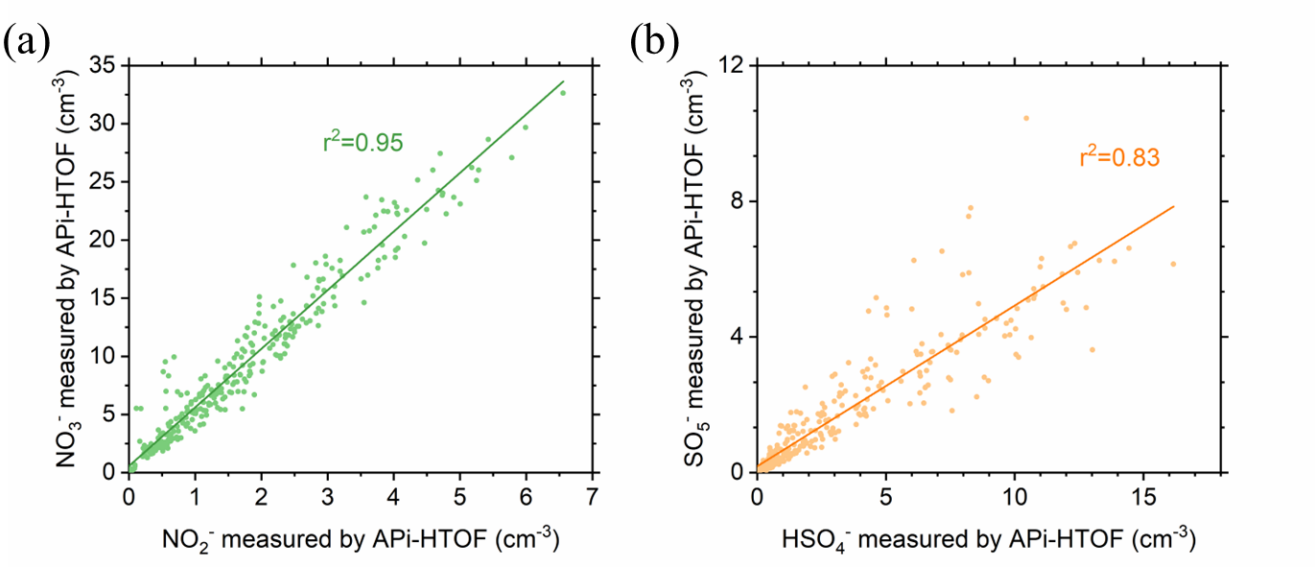

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54 **Figure S8**. The scatter plot of the concentrations of specific ions measured by APi-TOF in urban Beijing. (a) NO_2^- and NO_3^-;

55 (b) HSO_4^- and SO_5^-.

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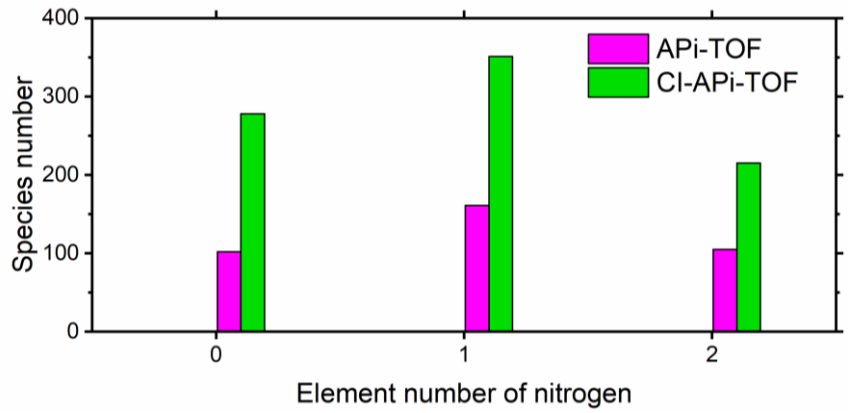

Figure S9. The number of nitrogen atoms contained in the organic molecules detected in APi-TOF and CI-APi-TOF in urban Beijing. Note that the nitrogen contained in NO_3^- is already subtracted from the formula.

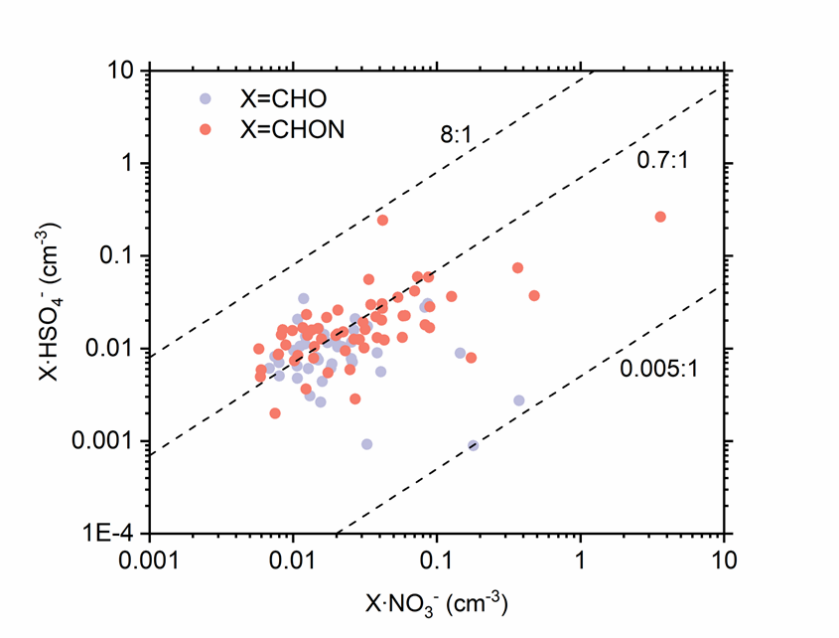

Figure S10. The comparison between the average concentration of the same organic molecules ionized by NO_3^- ($X{\cdot}NO_3^-$) and HSO_4^- ($X{\cdot}\ HSO_4^-$) during the observation in urban Beijing. 100 species were compared in total, including 41 CHO species and 59 CHON species.

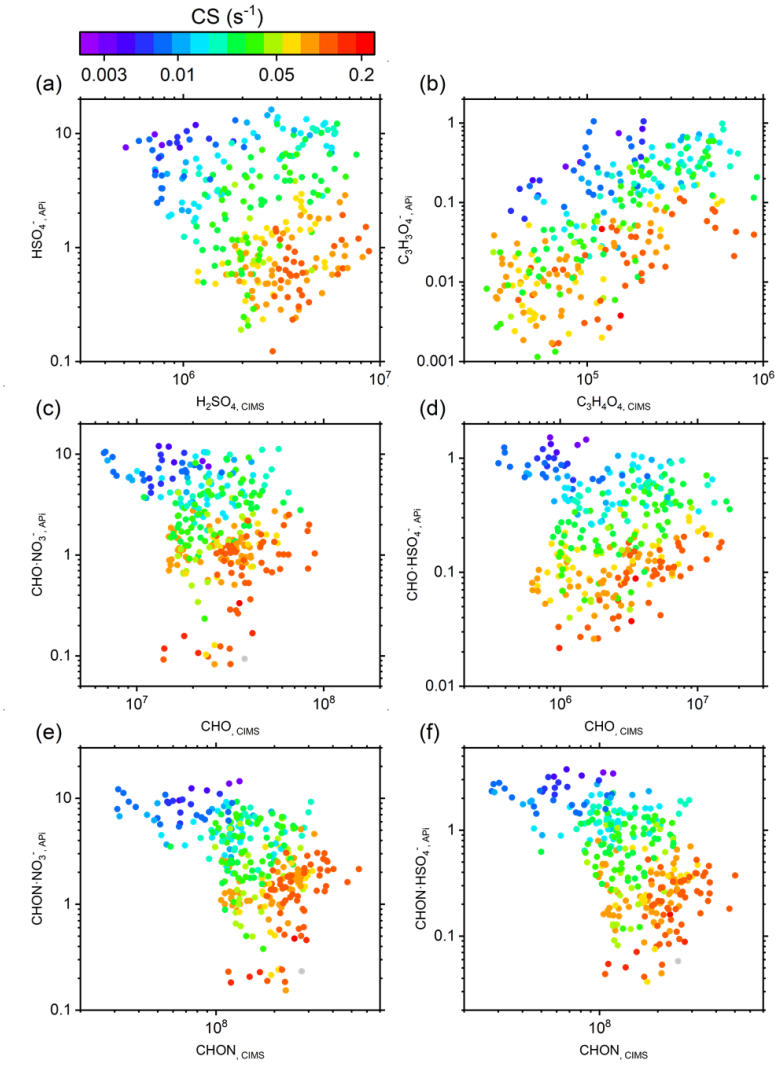

Figure S11. Scatter plots of the number concentrations of neutral molecules and the corresponding cluster ions, which are colored by CS in urban Beijing. From (a) to (f), the cluster ions are HSO_4^-, $C_3H_3O_4^-$, $CHONO_3^-$, $CHOHSO_4^-$, $CHONNO_3^-$, and $CHONHSO_4^-$ respectively. Their corresponding neutral molecules are H_2SO_4, $C_3H_4O_4$, CHO, and CHON respectively.

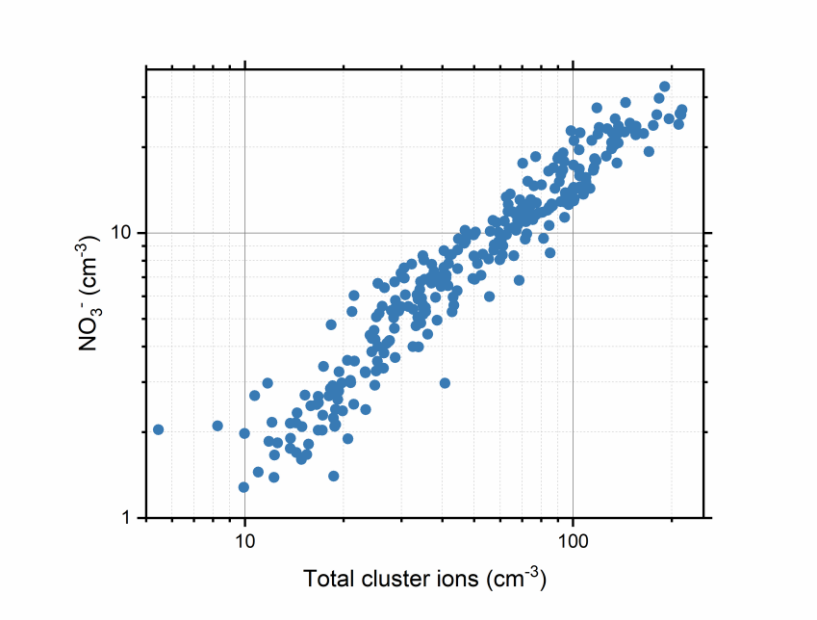

Figure S12. The scatter plot of concentration of total negative cluster ion concentrations and NO_3^- measured by APi-TOF in urban Beijing.

76 **Table S1.** The reduced mobilities of NO_3^-, HSO_4^-, and some of their clusters

Formula	m/z	Reduced mobility, K_0 ($cm^{-2}\cdot V^{-1}\cdot s^{-1}$)
O_2^-	31.9904	[a]3.28
NO_2^-	45.9935	[a]2.70
NO_3^-	61.9884	[b]2.45
$HNO_3\cdot NO_3^-$	124.9840	[c]2.07
HSO_4^-	96.9601	[d]2.01
$H_2SO_4\cdot HSO_4^-$	194.9275	[d]1.63
$(H_2SO_4)_2\cdot HSO_4^-$	292.8949	[d]1.27
$(H_2SO_4)_3\cdot HSO_4^-$	390.8622	[d]1.17
$(H_2SO_4)_2\cdot C_2H_7N\cdot HSO_4^-$	337.9527	[d]1.21

77 [a] From Spangler et al. (Spangler and Collins, 1975)； [b] From Stano et al. (Stano et al., 2008)； [c] From Liang et al. (Liang
78 et al., 2013)； [d] From Jen et al. (Jen et al., 2014)

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Reference

Jen, C. N., Hanson, D. R., and McMurry, P. H.: Toward Reconciling Measurements of Atmospherically Relevant Clusters by Chemical Ionization Mass Spectrometry and Mobility Classification/Vapor Condensation, Aerosol Sci. Technol., 49, i-iii, 10.1080/02786826.2014.1002602, 2014.

Krechmer, J. E., Groessl, M., Zhang, X., Junninen, H., Massoli, P., Lambe, A. T., Kimmel, J. R., Cubison, M. J., Graf, S., Lin, Y.-H., Budisulistiorini, S. H., Zhang, H., Surratt, J. D., Knochenmuss, R., Jayne, J. T., Worsnop, D. R., Jimenez, J.-L., and Canagaratna, M. R.: Ion mobility spectrometry–mass spectrometry (IMS–MS) for on- and offline analysis of atmospheric gas and aerosol species, Atmos. Meas. Tech., 9, 3245-3262, 10.5194/amt-9-3245-2016, 2016.

Liang, X., Zhou, Q., Wang, W., Wang, X., Chen, W., Chen, C., Li, Y., Hou, K., Li, J., and Li, H.: Sensitive detection of black powder by a stand-alone ion mobility spectrometer with an embedded titration region, Anal. Chem., 85, 4849-4852, 10.1021/ac400337s, 2013.

Spangler, G. E. and Collins, C. I.: Reactant ions in negative ion plasma chromatography, Anal. Chem., 47, 393-402, 10.1021/ac60353a019, 1975.

Stano, M., Safonov, E., Kucera, M., and Matejcik, S.: Ion Mobility Spectrometry Study of Negative Corona Discharge in Oxygen/Nitrogen Mixtures, Chem. Listy, 102, S1414-S1417, 2008.