

Structures and compositions of copper oxide cluster cations studied by ion mobility mass spectrometry

(Tohoku Univ.) ○ M. A. Latif, J. W. J. Wu, R. Moriyama, M. Nakano, K. Ohshimo, and F. Misaizu

[Introduction] Copper oxide clusters have been a subject of intense investigation in recent years due to an important role in catalytic reactions both oxidation [1] and reduction [2]. Physical and chemical properties of a specific catalyst largely depend on its size and structures. Therefore, it is important to know the geometrical structure and stability to evaluate catalytic activity of the nano-sized model, such as cluster in the gas phase. In this study, stable compositions and size-dependent structures of copper oxide cluster cations were investigated by ion mobility mass spectrometry (IM-MS), which is a powerful technique for identification and separation of cluster ions based on their mobility in carrier gas inside an ion-drift cell. Structural isomers, clusters of the same mass but different structures, can be identified by comparison between their collision cross sections (CCSs) measured by IM-MS and CCSs estimated by quantum chemical calculations.

[Experiment] IM-MS experiments were performed using a home-built IM-MS vacuum apparatus. Different series of copper oxide cluster cations, Cu_nO_m^+ , were generated by a combination of laser vaporization and supersonic expansion of O_2/He mixture gas. The generated cluster ions were injected into the ion-drift cell of ion mobility spectrometer (Figure 1) with kinetic energy of 50-250 eV by a pulsed electric field. Inside the drift cell, due to a balance of acceleration of ions by an electric field and deceleration by collisions

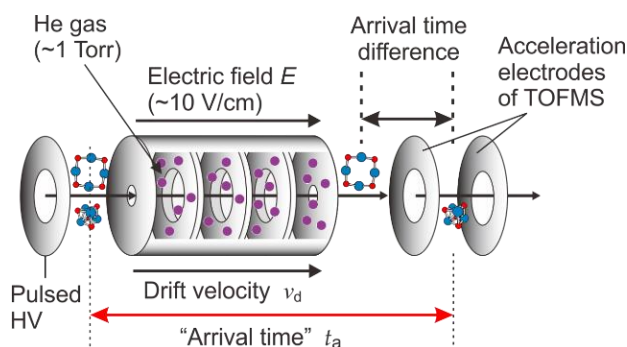


Figure 1. Ion-drift cell in IM-MS.

between cluster ions and buffer gas atoms, each cluster attains a constant drift velocity. The ions were reaccelerated by further pulsed voltage in an acceleration region of the time-of-flight (TOF) mass spectrometer at a given time later from the first pulse. The time duration between the first and the second pulses is defined as arrival time. The arrival time is almost equal to the time in which an ion spends in the cell, and thus it depends on the CCS of a specific cluster ion. Therefore, cluster ions with different CCSs reach the acceleration region of the TOF mass spectrometer at different arrival time. By obtaining TOF mass spectra at different arrival times, arrival time vs. TOF 2D plot were obtained.

[Results and Discussion] The compositions of Cu_nO_m^+ ($n \geq m$, up to $n, m = 9, 8$) were determined to be either oxygen-equivalent Cu_nO_n^+ , or oxygen-deficient like $\text{Cu}_n\text{O}_{n-1}^+$, $(\text{Cu}_2\text{O})_{n/2}^+$, and $(\text{CuO})(\text{Cu}_2\text{O})_{(n-1)/2}^+$ cluster ion series from TOF mass spectrum. Arrival time distributions (ATDs) were obtained from the IM-MS measurement in which the total ion intensity of certain TOF peak was shown as a function of arrival time (Figure 2). Most of the observed ATDs can be fitted with one Gaussian function. However, only for Cu_5O_4^+ , two Gaussian functions were necessary for the fitting. From these ATDs, experimental CCSs were estimated by applying kinetic theory of ion transport [3].

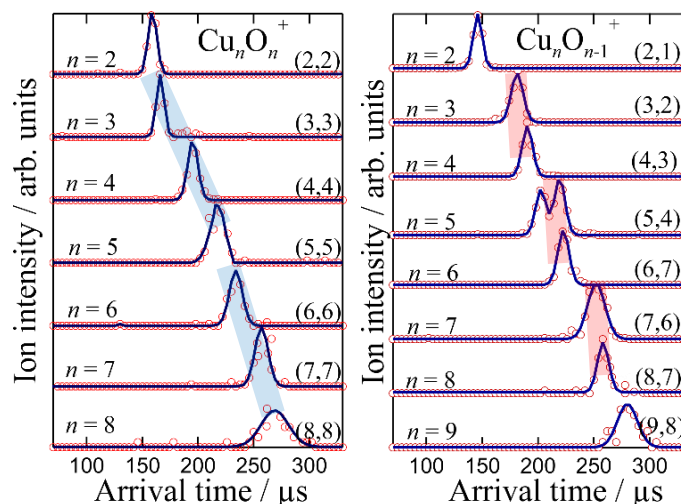


Figure 2. ATDs of Cu_nO_n^+ and $\text{Cu}_n\text{O}_{n-1}^+$ cluster cations.

On the other hand, some structures were calculated by B3LYP/cc-pVDZ level in Gaussian 09, and their CCSs were estimated by MOBCAL program [4]. Experimental and theoretical CCSs (Ω_{exp} , Ω_{calc}) are shown in Figure 3. Geometrical structures of the cluster ions were assigned by means of comparison between their experimental and theoretical CCSs. For Cu_nO_n^+ cluster ion, for $n = 3-5$, two dimensional (2D) ring and sheet-like structures, and for $n = 6-8$, 2D sheet and 3D compact structures were assigned. In the case of $\text{Cu}_n\text{O}_{n-1}^+$ cluster ion, stepwise structural growth was observed from 2D→3D for sizes Cu_3O_2^+ to Cu_4O_3^+ , Cu_5O_4^+ to Cu_6O_5^+ , and Cu_7O_6^+ to Cu_8O_7^+ . Additionally, for Cu_5O_4^+ , 2D sheet and 3D compact isomers were found to coexist (Figure 4).

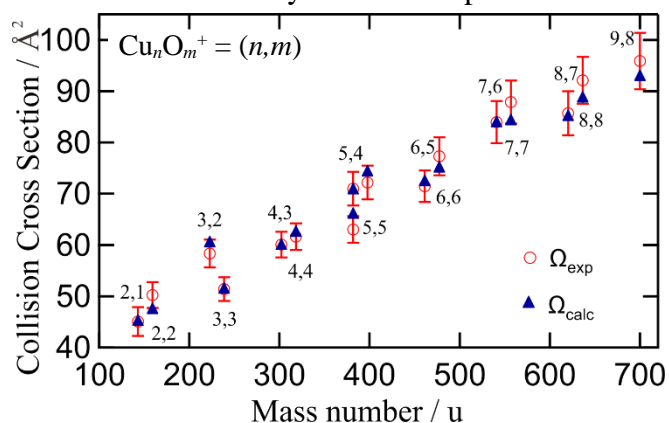


Figure 3. Experimental and theoretical CCSs.

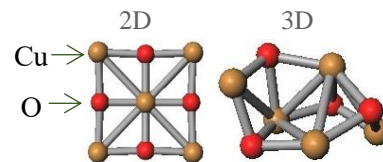


Figure 4. Structural isomers of Cu_5O_4^+ .

References

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