Letter to the Editor

Comments on "Identification of Negative Ion at *m/z* 20 Produced by Atmospheric Pressure Corona Discharge Ionization under Ambient Air"

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In this study,[1] OH^- and its hydrated ions $OH^-(H_2O)_n$ (n=1–4) were identified as major ions produced under ambient air atmospheric pressure corona discharge ionization. By the corona discharge ionization of air with moisture, OH^- should be readily formed by the decomposition of H_2O to form $OH^{\bullet}$ and subsequent electron attachment to $OH^{\bullet}$ in the air plasma. The resultant OH^- reacts with CO_2 that is a constituent of air with ~400 ppm by Eq. (1).

$$OH^- + CO_2 + M \rightarrow HCO_3^- + M, \text{ M: third body} \qquad (1)$$

Fehsenfeld and Ferguson measured the third-order rate constant of reaction (1) as k=7.6×10^{-28} cm^6 s^{-1} molecule^{-2} for M=O_2 at 296 K.[2] From this rate constant, the lifetime of reaction (1) to form HCO_3^- in air containing ~400 ppm of CO_2 is roughly estimated to be ~100 ps.[3] The transit time of primary ions generated at the ambient ion source to the ion sampling orifice in commercial instruments is roughly estimated to be 10 μs to ms depending on the distance between the two electrodes.[4] Therefore, OH^- ion should be almost completely converted to form HCO_3^- under the experimental conditions.[3] Thus, the $OH^-(H_2O)_n$ are highly unlikely to survive long in the atmospheric pressure ionization source. In addition, it is puzzling that $O_2^{-\bullet}$ (*m/z* 32), $O_3^{-\bullet}$ (*m/z* 48), $CO_3^{-\bullet}$ (*m/z* 60), and HCO_3^- (*m/z* 61), which are the major negative ions generated in the atmospheric pressure chemical ionization conditions, were barely detected.

The authors concluded that the ions at *m/z* 20 and 22 produced by the atmospheric pressure corona discharge ionization are $H_2O^{-\bullet}(H_2)$ and $HF^{-\bullet}(H_2)$, respectively. They described that electron affinity (EA) of the H_2O molecule is positive, according to the report of the estimation of the hydration energy of electron by Ballard.[5] Although an excess electron can be stabilized in bulk water, stable $H_2O^{-\bullet}$ is not produced in the electron attachment to an H_2O molecule in

gas phase. Therefore, multiple number of water molecules are needed to stabilize the excess electron. The formation of $(H_2O)_n^{-\bullet}$ has been experimentally demonstrated by the use of an extremely low-energy electron source and an electron can be captured by water clusters $(H_2O)_n$ with $n \geq 11$.[6] This observation suggests that the EA of $(H_2O)_n$ becomes positive, when n is larger than 11, although EA of $(H_2O)_n$ with n<11 is negative or even positive but a very small value. Indeed, the EAs of $(H_2O)_{11}$ and $(H_2O)_{19}$ are reported to be 0.75 and 1.12 eV,[6] suggesting that the EA of $(H_2O)_n$ increases with the increase in the number of H_2O molecules consisting the clusters. In contrast, the formation of $(H_2O)_n^{-\bullet}$ was reported by the collision between $(H_2O)_n$ and Rydberg atom.[7] In this method, $(H_2O)_n^{-\bullet}$ with n=2, 6, and 7 are predominantly observed species below n<11.[8] The EA of $(H_2O)_2$ is calculated as 0.0356 eV,[9] which is much smaller than that of $(H_2O)_{11}$ and $(H_2O)_{19}$. Regarding the small water cluster anion, an excess electron is present in the Rydberg orbital, and the vertical detachment energy of $(H_2O)_n^{-\bullet}$ decreases with decrease in the number of H_2O molecules consisting the clusters.[10] In the case of the smallest water cluster anion, $(H_2O)_2^{-\bullet}$, the vertical detachment energy is only 0.0286 eV.[10] Consequently, the small water cluster anion would immediately react with atmospheric components in the ambient condition due to their low stability.

As in the case of H_2O, it is well known that H_2, and HF molecules do not form stable negative ions, *i.e.*, EAs of these molecules are negative. Although detailed property of $H_2O^{-\bullet}(H_2)$ and $HF^{-\bullet}(H_2)$ has not been investigated, these ions are suggested to be short-lived anion species in ambient condition, as expected from number of molecules consisting of the clusters. In fact, no negative ions were detected with *m/z* values lower than 32 ($O_2^{-\bullet}$) in ambient air corona discharge ionization reported by Hiraoka and co-workers.[11] Thus, we would like to raise a question: Why could these short-lived

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species such as $OH^-(H_2O)_n$ (n=0–4), $H_2O^{-\bullet}(H_2)$, and $HF^{-\bullet}(H_2)$ be detected while the stable ions such as $O_2^{-\bullet}$, $O_3^{-\bullet}$, $CO_3^{-\bullet}$, and HCO_3^- were barely detected in ambient air corona discharge ionization source? $OH^-(H_2O)_n$ and $(H_2O)_n^{-\bullet}$ are reported to be formed by irradiating electrons with neutral water cluster in adiabatic expansion.[12,13] These short-lived species might be produced from the reaction of water clusters and low energy electrons produced by corona discharge in the orifice-skimmer region. Are these ions detected by the mass spectrometer quipped with different ion sampling optics?

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