Experimental Confirmation of SrF(CH_{3}F)_{0-4}^{+} and SrF(H_{2}O)(CH_{3}F)_{0-3}^{+} Cluster Ions Generated in the Reaction-cell of ICP-QMS/QMS

Yanbei ZHU, Kazumi NAKANO, and Yasuyuki SHIKAMORI

*National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan
**Agilent Technologies Japan, Ltd., 9-1 Takakura, Hachioji, Tokyo 192-8510, Japan

Multiple unknown high-order cluster ions were observed as the results of ion-molecule reactions between strontium ions and fluoromethane molecules in the reaction-cell of an inductively coupled plasma tandem quadrupole mass spectrometer (ICP-QMS/QMS). In order to elucidate the structures of these unknown cluster ions, isotope-enriched fluoromethane (CD_{3}F) was used as the reaction-cell gas compared to natural fluoromethane (CH_{3}F). As results, SrF(CH_{3}F)_{0-4}^{+} and SrF(H_{2}O)(CH_{3}F)_{0-3}^{+} cluster ions were experimentally confirmed in the present work. While SrF(H_{2}O)(CH_{3}F)_{0-3}^{+} cluster ions in the reaction-cell of ICP-QMS/QMS were observed and confirmed for the first time in the world.

**Keywords** ICP-QMS/QMS, reaction-cell, cluster ion, CD_{3}F

(Received June 28, 2017; Accepted July 5, 2017; Published August 10, 2017)
of \(^{87}\text{Sr}^{19}\text{F}\), \(^{87}\text{Sr}^{20}\text{F}_2\), \(^{87}\text{Sr}^{21}\text{F}_2\) and \(^{87}\text{Sr}^{22}\text{F}_2\) respectively. All of these species have been covered by a report by Zhao et al.\(^{11}\). The \(m/z\) of peaks No. 8 and 10 were 208 and 242, respectively. These peaks could be assigned to the species of \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_3^{+}\) and \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_4^{+}\), respectively, which were not covered by the report by Zhao et al.\(^{11}\) but were also observed in the present experiment. These results showed that \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_n^{+}\) were observed in the present experiment, i.e. the M mentioned above was \(^{87}\text{Sr}^{19}\text{F}\).

The species of \(^{87}\text{Sr}(\text{CD3F})_n\)\(^{+}\) reported by Zhao et al.\(^{11}\) were not observed in the present experiment, which should give \(m/z\) values of 121 and 155, respectively. In contrast, the peaks of No. 3, 5, 7, and 9 were observed with \(m/z\) values of 124, 158, 192, and 226, respectively. The \(m/z\) of the M’ mentioned above was 124, i.e. a species having relative molecular mass of 37 in addition to \(^{87}\text{Sr}^{+}\).

Taking into consideration the fact that the starting ions and molecules in the present experiment were \(^{87}\text{Sr}^{+}\) and \(^{12}\text{C}\text{H}_3^{19}\text{F}\), respectively, a relative molecular mass of 37 might be partly attributed to the species of \(^{19}\text{F}\) or \(^{12}\text{C}\text{H}_3^{19}\text{F}\). Therefore, CD3F was used as the reaction-cell gas in order to elucidate the species. If the above-mentioned species with a relative molecular mass of 37 was related to \(^{19}\text{F}\), the \(m/z\) of peak No. 3 will stay at 124 with CD3F as the reaction-cell gas. In contrast, the peaks of No. 5, 7, and 9 were observed with \(m/z\) values of 124, 158, 192, and 226, respectively. The \(m/z\) of the M’ mentioned above was 124, i.e. a species having relative molecular mass of 37 in addition to \(^{87}\text{Sr}^{+}\).

The results of product ions generated by \(^{87}\text{Sr}^{+}\) and CD3F are plotted in Fig. 2. In comparison to Fig. 1, it can be seen from Fig. 2 that the peaks of No. 1, 2, and 3 were also observed with CD3F as the reaction gas. The peaks related to \(^{12}\text{C}\text{H}_3^{19}\text{F}\), i.e. No. 4 to No. 10, in Fig. 1 are not observed in Fig. 2. It is notable that peak No. 3 can also be observed in Fig. 2 at the lower \(m/z\) side of their neighboring dominant peaks. These secondary peaks might be attributed to the partly replacement of \(^{12}\text{C}\) by \(^{2}\text{D}\) in \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_0^{+}\) and \(^{87}\text{Sr}^{19}\text{F}(\text{H}_2\text{O})(\text{CD3F})_3^{+}\). One of the reasons for this replacement might be attributed to impurities in the reaction gas.

The dependence of the signal intensities of the above-mentioned dominant peaks were investigated at various flow rates of the reaction-cell gas. The results for each peak were normalized compared to its maximum signal intensity. The results of the relative signal intensities of each peak of \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_n^{+}\) and \(^{87}\text{Sr}^{19}\text{F}(\text{H}_2\text{O})(\text{CD3F})_3^{+}\) are plotted in Figs. 3(a) and 3(b).

It can be seen from Figs. 3(a) and 3(b) that the larger is \(m/z\) of a peak, the higher is the reaction-cell gas-flow rate required to obtain the maximum relative signal intensity. These results indicate that the mechanisms for producing cluster ions of \(^{87}\text{Sr}^{19}\text{F}(\text{CD3F})_n^{+}\) and \(^{87}\text{Sr}^{19}\text{F}(\text{H}_2\text{O})(\text{CD3F})_3^{+}\) could be expressed by Eqs. (1) to (9), respectively:

\(^{87}\text{Sr}^{+} + ^{12}\text{C}\text{D}_3^{19}\text{F} \rightarrow ^{87}\text{Sr}^{19}\text{F}^{+} + ^{12}\text{C}\text{D}_3^{19}\text{O}, \quad (1)\)

\(^{87}\text{Sr}^{19}\text{F}^{+} + ^{12}\text{C}\text{D}_3^{20}\text{F} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{20}\text{F})^{+}, \quad (2)\)

\(^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{20}\text{F})^{+} + ^{12}\text{C}\text{D}_3^{21}\text{F} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{22}\text{F})^{+}, \quad (3)\)

\(^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{22}\text{F})^{+} + ^{12}\text{C}\text{D}_3^{23}\text{F} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{23}\text{F})^{+}, \quad (4)\)

\(^{87}\text{Sr}^{+} + ^{12}\text{C}\text{D}_3^{19}\text{O} \rightarrow ^{87}\text{Sr}^{19}\text{F}^{+} + ^{12}\text{C}\text{D}_3^{19}\text{O}, \quad (5)\)

\(^{87}\text{Sr}^{19}\text{F}^{+} + ^{12}\text{C}\text{D}_3^{20}\text{O} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{20}\text{O})^{+}, \quad (6)\)

\(^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{20}\text{O})^{+} + ^{12}\text{C}\text{D}_3^{21}\text{O} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{22}\text{O})^{+}, \quad (7)\)

\(^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{22}\text{O})^{+} + ^{12}\text{C}\text{D}_3^{23}\text{O} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{23}\text{O})^{+}, \quad (8)\)

\(^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{23}\text{O})^{+} + ^{12}\text{C}\text{D}_3^{24}\text{O} \rightarrow ^{87}\text{Sr}^{19}\text{F}(^{12}\text{C}\text{D}_3^{24}\text{O})^{+}, \quad (9)\)
Table 1: Correlation between the signal intensities of each ionic species and the concentration of strontium$^{ab}$

| Sr concentration/ µg L$^{-1}$ | 87 | 106 | 124 | 143 | 161 | 180 | 198 | 217 | 235 | 254 |
|-----------------------------|----|----|----|----|----|----|----|----|----|----|
| 0.0                         | 571(8.9) | 119(17.7) | 2(108.7) | 8(67.4) | 2(100.0) | 3(83.9) | 3(104.6) | 4(70.7) | 2(141.4) | 3(156.9) |
| 24.9                        | 26001(2.5) | 25641(2.4) | 132(16.4) | 2081(1.9) | 315(9.8) | 2275(2.9) | 1973(4.9) | 5838(2.4) | 1231(4.6) | 1689(3.8) |
| 48.8                        | 47851(2.0) | 47701(2.6) | 275(9.1) | 3948(4.6) | 632(2.8) | 4233(2.4) | 3843(4.5) | 10855(2.0) | 2348(4.3) | 3263(3.7) |
| 98.5                        | 98582(1.5) | 99189(2.3) | 570(8.3) | 8048(4.0) | 1274(2.3) | 8778(2.6) | 7774(4.1) | 22856(1.8) | 5072(3.7) | 6886(2.8) |
| $R^2$                       | 0.9996 | 0.9996 | 0.9993 | 0.9999 | 0.9999 | 0.9996 | 1.0000 | 0.9994 | 0.9987 | 0.9994 |

$^a$ Reaction-cell gas, 0.25 mL CD$_3$F min$^{-1}$. $^b$ The value in the brackets following each signal intensity is its relative standard deviation (unit, %).

The increase of the reaction-cell gas flow rate resulted in the progress of each reaction of Eqs. (1) to (9). It is notable that the relative signal intensities of every peak decreased apparently when the reaction-cell gas flow rate exceeded 0.4 mL min$^{-1}$, which could be attributed to a loss of the transport efficiency through the reaction-cell due to increased collision opportunities.

It is notable that, as is shown in Fig. 3(a), the dominant signals of SrF(CH$_3$F)$_{0-4}$+ shifted linearly to larger molecular species at a higher CD$_3$F flow rate. In contrast, as is shown in Fig. 3(b), those of SrF(H$_2$O)(CH$_3$F)$_{0-3}$+ shifted nonlinearly to larger molecular species. These results indicate that the source of (H$_2$O)$^+$ in the cluster ions was not the impurity in the CD$_3$F cell gas, but the residual impurity in the CD$_3$F cell gas, but the residual.

The dependence of the signal intensities of SrF(CD$_3$F)$_{0-4}$+ and SrF(H$_2$O)(CD$_3$F)$_{0-3}$+ on the concentrations of strontium in the standard solutions was investigated with a reaction-cell gas flow rate of 0.25 mL CD$_3$F min$^{-1}$. The results are summarized in Table 1, in which the squares of the correlation factor ($R^2$) between the signal intensities and the concentrations of strontium are also summarized. It can be seen from Table 1 that the signal intensity of each ionic species was linearly dependent on the concentrations of strontium, giving a $R^2$ value close to or over 0.9990. It should be pointed out that the sensitivities of ionic species with an $m/z$ value of 124 and 161 were much lower than those of other species. Even though, the present results indicate that each ionic species might be used for quantification of the strontium concentration in the solution introduced into the ICP-QMS/QMS.

In the present work, ionic species of SrF(CH$_3$F)$_{0-4}$+ and SrF(H$_2$O)(CH$_3$F)$_{0-3}$+ cluster ions were experimentally confirmed by an ICP-QMS/QMS with an octopole reaction-cell. This is the first report concerning the generation of SrF(CH$_3$F)$_{0-4}$+ and SrF(H$_2$O)(CH$_3$F)$_{0-3}$+ species in the reaction-cell of ICP-MS. The application of $^3$D enriched fluoromethane (CD$_3$F) helped to confirm the structure of related unknown species generated in the reaction-cell of ICP-QMS/QMS. The increase of the reaction-cell gas flow rate benefitted for the generation of ionic species having more reaction-cell molecules in its structure. The signal intensity of each ionic species of SrF(CD$_3$F)$_{0-4}$+ and SrF(H$_2$O)(CD$_3$F)$_{0-3}$+ depended on the concentration of strontium, and might be used for the quantitation of strontium.

References

1. S. D. Tanner, V. I. Baranov, and D. R. Bandura, Spectrochim. Acta, Part B, 2002, 57, 1361.
2. D. W. Koppenaal, G. C. Eiden, and C. J. Barina, J. Anal. At. Spectrom., 2004, 19, 561.
3. J. Takahashi and N. Yamada, Bunseki Kagaku, 2004, 53, 1257.
4. N. Yamada, Spectrochim. Acta, Part B, 2015, 110, 31.
5. D. R. Bandura, V. I. Baranov, A. E. Litherland, and S. D. Tanner, Int. J. Mass Spectrom., 2006, 255-256, 312.
6. P. J. Gray and J. W. Olesek, Spectrom. Acta, Part B, 2015, 105, 60.
7. L. J. Moens, F. P. Vanhaecke, D. R. Bandura, V. I. Baranov, and S. D. Tanner, J. Anal. At. Spectrom., 2001, 16, 991.
8. P. Cheng, G. K. Koyanagi, and D. K. Bohme, Anal. Chim. Acta, 2008, 627, 148.
9. E. Bolea-Fernadez, L. Balcaen, M. Resano, and F. Vanhaecke, J. Anal. At. Spectrom., 2016, 31, 303.
10. G. K. Koyanagi, X. Zhao, V. Blagojevic, M. J. Y. Jarvis, and D. K. Bohme, Int. J. Mass Spectrom., 2005, 241, 189.
11. X. Zhao, G. K. Koyanagi, and D. K. Bohme, J. Phys. Chem. A, 2006, 110, 10607.
12. L. Balcaen, D. Bolea-Fernadez, M. Resano, and F. Vanhaecke, Anal. Chim. Acta, 2014, 809, 1.