Structural Analysis of $(AXA')^+$ Ion in Gas Phase by ab initio MO Calculations

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A stable triple ion, $(AXA')^+$ [A, A' = alkali metal atoms; X = halogen atom] was identified by fast atom bombardment (FAB) mass spectrometry (MS). It is interesting for scientists in secondary ionization mass spectrometry (SIMS) and MS to determine whether the structure of the ion $(AXA')^+$ in vacuum is linear or triangle. We will, then, examine the existence and structure of the triple $(NaClK)^+$ and $(NaBrK)^+$ ions from the stabilization energies using ab initio Hartree-Fock MO calculations with 6-311G* bases. We suggest from the calculations that the linear structure of the ions is more stable, and the triangle is also stable, since stabilization energies of both linear and triangle structures for $(NaClK)^+$ and $(NaBrK)^+$ ions were obtained as (-692.8, -688.5) and (-669.2, -664.2) kJ/mol, respectively.

1. Introduction

Fuoss and co-worker [1] had proposed the existence of the triple ion in low dielectric constant media. After that, the triple positive and negative ion aggregates, such as $(LiXLi)^+$ and $(XLiX)^-$ ions in the condensed phase were also suggested from analysis of the concentration-dependent frequency shifts in Raman spectra [2]. On the other hand, Isa and co-workers were very interested in the existence of the triple ions in gas phase using fast atom bombardment mass spectrometry (FABMS) method, after the ions were formed in concentrated electrolyte solutions. They, then, measured the triple $(AXA')^+$ ions and the correlated ions by FABMS method, and, furthermore, fragmented the positive ions with tandem mass spectrometry (MS/MS) [3]. In the collisionally activated dissociation (CAD) spectra of the triple $(AXA')^+$ ion, they observed the A^+, $(A')^+$, AX^+, $A'X^+$, X^+, and $(AA')^+$ ions [4]. They, thus, assumed that all $(AXA')^+$ ions are not only linear, but also partly triangle, because $(AA')^+$ ion is obtained in the CAD spectrum. Then, in the present work, we aim to clarify the existence and structure of the triple $(AXA')^+$ ions in gas phase from ab initio MO calculations.

As a fundamental investigation, it is very important for scientists in secondary ionization mass spectrometry (SIMS), and MS to provide information on the existence and structure of the ions in gas phase. So far as we know, there is no work for such investigation from a theoretical viewpoint. Here we demonstrate the existence and structure of the triple ions $(NaClK)^+$ and $(NaBrK)^+$ from the stabilization energy using the Hartree-Fock (HF) SCF MO method.

2. Experimental

The mass spectra were obtained with a Jeol DX 303 EBE type (E and B represent electro-static and magnetic sectors, respectively) double-focusing mass spectrometer and a DA 5000 data system. The triple ions $(AXA')^+$ were generated by FAB ionization using argon as the bombarding gas with an atom gun energy of 6 keV and a FAB gun emission current of approximately 20 mA. In the collisionally activated dissociation (CAD) unit (10^{-7}mbar), a triple $(AXA')^+$ ion at the high energy collides with an argon atom at the static state, is divided into several ions, and the ions travel independently without the recombination of the ions. Then we can observe A^+, $(A')^+$, AX^+, $A'X^+$, X^+, and $(AA')^+$ ions in the next MS unit. Fig. 1 b) showed fragment ions (Na^+, K^+, NaK^+, Br^+, $NaBr^+$, and KBr^+) in the CAD spectrum of the triple $(NaBrK)^+$ ion. We can thus assume that all $(NaBrK)^+$ ions are not only linear, but also partly triangle, because the NaK^+ ion was obtained in the CAD spectrum.

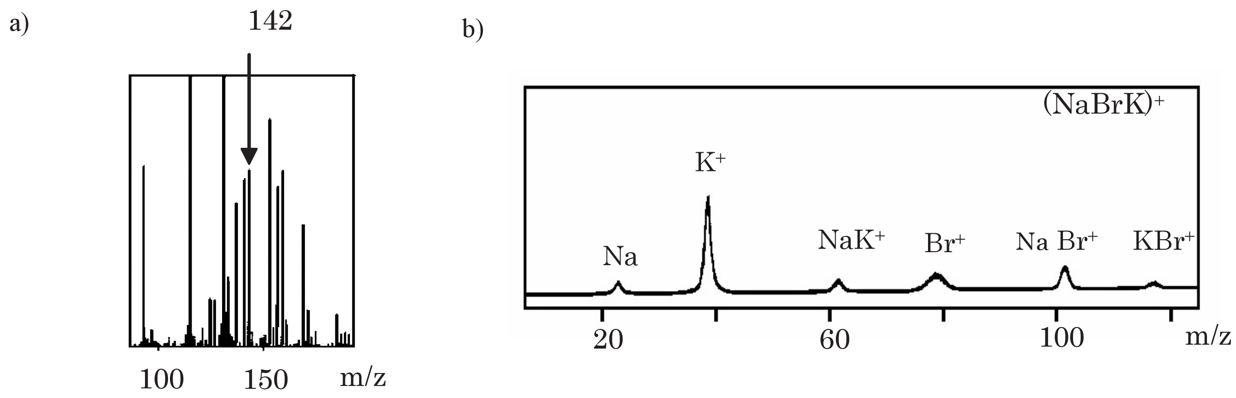

Fig. 1. a) (NaBrK)$^+$ ion mass spectrum in the range of 100 ~ 200 m/z. **b)** Fragment ions (Na$^+$, K$^+$, NaK$^+$, Br$^+$, NaBr$^+$, and KBr$^+$) in the CAD spectrum of the triple (NaBrK)$^+$ ion.

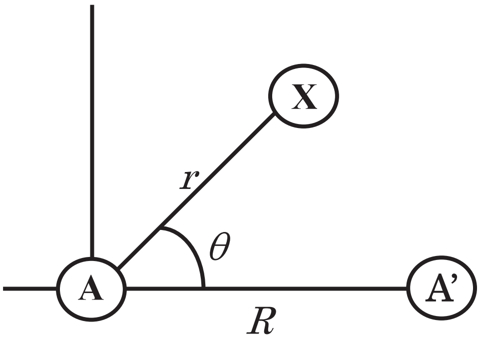

Fig. 2. Geometrical arrangement of the triple ion interaction system for the A$^+$X$^-$ vector to the A$^+$(A')$^+$ axis vector. The lengths of the A$^+$X$^-$, and the A$^+$(A')$^+$ axis vectors were set as r and R, and the angle between the A$^+$X$^-$ vector and the A$^+$(A')$^+$ axis vector as θ .

3. Computational Details

All calculations were performed by ab initio Hartree-Fock (HF) MO calculations with 6-311G* bases in GAUSSIAN 94 program [5]. The geometric structures of the triple (AXA')$^+$ ions are given by considering a crystal plane of the octahedral rock-salt structure. Fig. 2 shows the geometrical arrangement of the triple ion interaction system for the A$^+$X$^-$ vector to the A$^+$(A')$^+$ axis vector. We defined the lengths of the A$^+$X$^-$, and the A$^+$(A')$^+$ axis vectors as r and R, and the angle between the A$^+$X$^-$ vector and the A$^+$(A')$^+$ axis vector as θ. For the interaction system, we estimated the total energies of the triple ions with varying the intermolecular distances, r and R and the angle, θ in the HF SCF calculations.

In the minimum point of the total energy for each interaction system, we obtained the stabilization energy, ΔE, in the following equation;

$$\Delta E = E_{(AXA')^+} - E_{(A^+ + (A')^+ + X^-)} \qquad (1)$$

where $E_{(AXA')^+}$ and $E_{(A^+ + (A')^+ + X^-)}$ denote the total energy of the triple ion, and sum of the total energy for each ion, respectively. We defined the energy in the atomic unit (a.u.) (1.0000 a.u. = 27.211 eV = 2625.19 kJ/mol).

4. Results and Discussion

In order to determine the existence and structure of the triple (NaBrK)$^+$ and (NaClK)$^+$ ions from the stabilization energy using Hartree-Fock (HF) SCF MO method, we first calculated total energies of individual ions in Table 1. Furthermore, we considered the geometrical arrangement in Fig. 2, to obtain the stabilization energies. Fig. 3 shows the three-dimensional potential surfaces of the total energy axis to the axes of the intermolecular distance r and angle θ between the A^+X^- vector and the $A^+(A')^+$ axis at R = 5.4Å for the triple $(NaBrK)^+$ ion. In the figure, we can see the minimum point in the potential surface of -3333.36 a.u. in the interatomic distance of 2.6 Å, and at the angle of 0°. From similar calculations, we showed the minimum total energies and the stabilization energies of the triple $(NaBrK)^+$ and $(NaClK)^+$ ions at the interatomic distances, (*R* and *r*), and the angle, θ in Table 2. The largest stabilization energies of the linear types for the triple $(NaBrK)^+$ and $(NaClK)^+$ ions were estimated as -0.2549 a.u. (-669.2 kJ/mol), and -0.2639 a.u.(-692.8 kJ/mol), respectively. On the other hand, we obtained the stabilization energies of the trianglar types as about (-664.2~ -654.0) and (-688.5 ~ -674.4) kJ/mol, respectively. Those stabilization energies are much larger than chemi-sorption energy (-85~ -420 kJ/mol), physical adsorption energy (-42 kJ/mol), and hydrogen-bond energy (-5.4~ -34 kJ/mol). Thus, we can confirm that the linear and triangle structures for the ions are very stable from the calculated energies. This corresponds to the experimental analysis for the existence of both linear and triangle structures of the stable triple ion, $(AXA')^+$.

Table 1. Total energies of individual ions for $(AXA')^+$ in Hartree-Fock MO calculations with 6-311G* bases.

Ion	Total Energy (a.u.)
Na^+	-161.66423
K^+	-599.00189
Cl^-	-459.56405
Br^-	-2572.43740
$Na^++K^++Cl^-$	-1220.23017
$Na^++K^++Br^-$	-3333.10352

1.0000 a.u. = 27.211 eV = 2625.19 kJ/mol

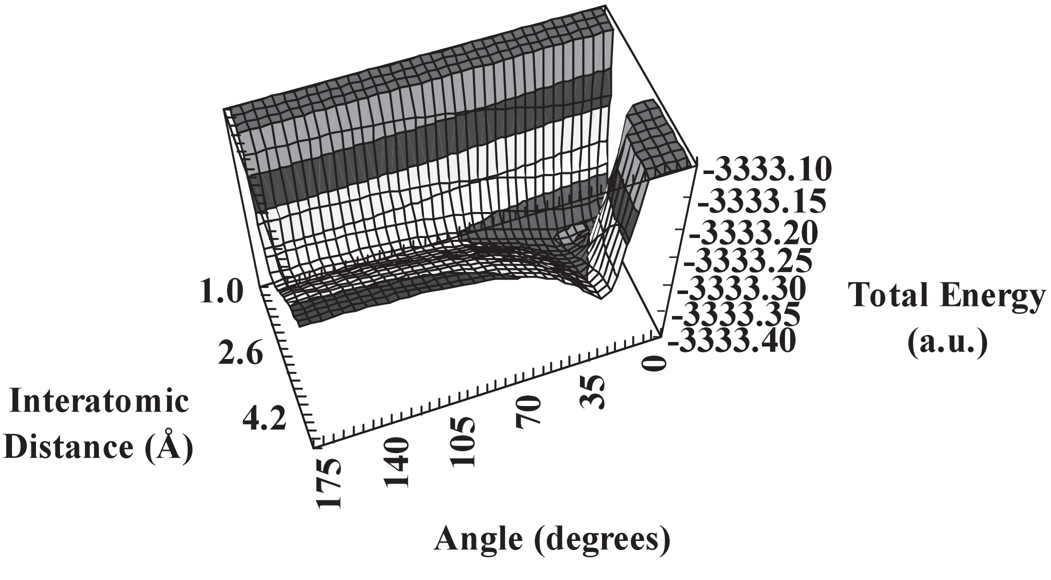

Fig. 3. Three-dimensional potential energy surface to the axes of the intratomic distance *r* and the angle θ at *R* = 5.4 Å for the $(NaBrK)^+$ ion.

Table 2. Total and stabilization energies of the triple $(AXA')^+$ ions in Hartree-Fock MO calculation with 6-311G* bases.

$(AXA')^+$ ions	R (Å)	r (Å)	θ (degrees)	Total Energy (a.u.)	Stabilization Energy (a.u.)	(kJ/mol)
$(NaBrK)^+$						
	5.0	2.6	30	-3333.35262	-0.24910	-654.01
	5.2	2.6	25	-3333.35467	-0.25115	-659.39
	5.4	2.6	15	-3333.35650	-0.25298	-664.20
	5.6	2.6	0	-3333.35814	-0.25462	-668.50
	5.8	2.7	0	-3333.35841	-0.25489	-669.21
	6.0	2.7	0	-3333.35687	-0.25335	-665.17
$(NaClK)^+$						
	4.8	2.4	25	-1220.48702	-0.25685	-674.36
	5.0	2.4	20	-1220.48970	-0.25953	-681.39
	5.2	2.4	5	-1220.49242	-0.26225	-688.54
	5.4	2.5	0	-1220.49406	-0.26389	-692.84
	5.6	2.6	0	-1220.49305	-0.26288	-690.19
	5.8	2.6	0	-1220.49061	-0.26044	-683.78

5. Conclusions

We determined the existence and structure of the triple $(NaBrK)^+$ and $(NaClK)^+$ ions in gas phase from the stabilization energy using Hartree-Fock (HF) SCF MO method.

We obtained the largest stabilization energies of the linear types as -669.2, and -692.8 kJ/mol for the triple $(NaBrK)^+$ and $(NaClK)^+$ ions, res-pectively. On the other hand, the stabilization energies of the trianglar types for the triple $(NaBrK)^+$ and $(NaClK)^+$ ions are obtained as about (-664.2 ~ -654.0) and (-688.5 ~ -674.4) kJ/mol, respectively. Thus, we conclude that the linear and triangle structures of the ions in gas phase exist.

References

[1] R. M. Fuoss, C. A. Kraus, J. Am. Chem. Soc., **55**, 2387(1933).

[2] P. Petersen, P. Jacobsson, L. M. Torell, Electrochim. Acta **37,** 1495 (1992).

[3] K. Isa and Y. Takeuchi, Org. Mass Spectrom. **24,** 153 (1989).

[4] N. Martinez, K. Isa, R. Nakata, K. Endo J. Mass Spectrom. Soc. Jpn. 49,51(2001).

[5] M. J. Frisch, G. M. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Ceeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al- Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J.Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacomb, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andress, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Had-Gordon, C. Gonzalez, and J. A. Pople, GAUSSIAN 94, Revision C. 2, Gaussian, Pittsburgh, PA. 1995.

Excerpt from the discussions with the reviewers, added by the editor (in Japanese)

Reviewer： 用いられているTriple ionという言葉は一般的でしょうか？今ひとつ違和感があり，three atom ionなどの方がぴんと来ます．普通に用いられているのであれば，問題ありません．

Authors： triple ionという表現は 化学系で普通に用いられています．

Reviewer： 3.Table.2で示すstabilization energyですが，linearが最も安定化しています．それに対して，それほど値が変わらないのでtriangleのものもあるということが言いたいのだと思いますが．この手の理論計算では，相対的な安定構造の順位は良いとして，絶対的な安定エネルギーは議論しづらいという印象があります．そういう意見に対して，十分応えうる根拠がありますか？この辺の記述を加えた方が良いのではないでしょうか？

Authors： この計算で得られた安定化エネルギーの値 －650 ～ －700（kJ/mol）は同様に得られる計算値やまた実験から得られる化学吸着エネルギー(-85～ -420 kJ/mol)，物理吸着エネルギー(-42 kJ/mol)及び水素結合エネルギー(-5.4～ -34 kJ/mol)等より充分大きいので絶対的なものとして対応させることができます． そこで以下のような文章を本文に書き加えなどして直しました．
Those stabilization energies are much larger than chemisorption energy (-85~ -420 kJ/mol), physical adsorption energy (-42 kJ/mol), and hydrogen-bond energy (-5.4~-34 kJ/mol). Thus, we can confirm that the linear and triangle structures for the ions are very stable from the calculated energies.

Reviewer： CADは，イオンを希ガスなどと衝突させることでフラグメント化する方法であると認識しています．元々の構造がLinearだとしても，分子との衝突により構造が変化し，その後フラグメント化するという過程は考えられないのでしょうか？あるとすると，計算自身に意味がないことになってしまいます．衝突前の構造が保持される根拠となるものがあれば書き加えた方が良いのではないでしょうか？

Authors： CADにおける説明が充分でなかったかもしれません．そこで以下のように書き直しました．
In the collisionally activated dissociation (CAD) unit (10-7 mbar), a triple $(AXA')^+$ ion at the high energy collides with an argon atom at the static state, is divided into several ions, and the ions travel independently without the recombination of the ions. Then we can observe A^+, $(A')^+$, AX^+, $A'X^+$, X^+, and $(AA')^+$ ions in the next MS unit.

Reviewer： 本論文はイオンの構造をMO計算で調べたものであり，結果は明確でありかつ意味のあるものであると考えるため，掲載を推奨いたします．しかしながら，本論文は”Surface Analysis”には直接関係ありません．表面分析で用いるイオンの形態を議論したものであり，このジャーナルの分野を広くとらえるのであれば問題ないと思いますが，編集委員会でご判断下さい．

Authors： 丁寧なコメントを有り難うございました．
この研究で意図するところが一寸分かりにくかったかも知れません．そこで各箇所に関して，指摘されたところも考慮して書き直しました．
この研究でSurface Scienceに関連するのは SIMS関係の分野の方だと思います．
そこで 意図してabstractとintroductionに以下のような文に書き直しました．
"It is an interesting thing for scientists in secondary ionization mass spectrometry (SIMS) and MS to determine whether the structure of the ion $(AXA')^+$ in vacuum is linear or triangle."