Structural isomers of $(NO_2)_3^+$ by time-of-flight mass spectrometry and geometry optimization

([1]*School of Science, The University of Tokyo*, [2]*NTT Advanced Technology Corporation*, [3]*International Center for Young Scientists, National Institute for Materials Science*, [4]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Ramia Katori[1], Erik Lötstedt[1], Hiroki Mashiko[2], Seigo Nakamura[1], Atsushi Iwasaki[1], Takashi Hiroi[3], Kana Yamada[1], Toshiaki Ando[1], Shinichi Fukahori[4], Ryuto Kimura[1], Kaoru Yamanouchi[1]

Keywords: nitrogen dioxide, cluster ions, time-of-flight mass spectroscopy, isomerization

It has been reported that $(NO_2)_n^+$ cluster ions are generated when a mixed gas of Ar and NO_2 is irradiated with an electron beam or an Ar lamp, and that the yield of $(NO_2)_n^+$ is enhanced when n is odd.[1] The cluster ions of $(N_2O_4)_mNO_2^+$ are considered to be formed by dissociative ionization of the N_2O_4 moiety, $N_2O_4 + h\nu \rightarrow NO_2 + NO_2^+ + e^-$, within a neutral cluster of $(N_2O_4)_{m+1}$. However, the geometrical structure of $(NO_2)_n^+$ cluster ions has not been previously determined experimentally or discussed theoretically. By mass spectrometry, we have confirmed that $(NO_2)_n^+$ ($1 \leqq n \leqq 11$) are produced and that the yields of cluster ions, $(NO_2)_n^+$, having an odd number of NO_2 (n = odd), and $NO(NO_2)_n^+$ and $(NO)_2(NO_2)_n^+$, in which one and two oxygen atoms are lost from $(NO_2)_n^+$, are enhanced. These findings are consistent with those reported in the previous study.[1] To estimate their geometrical structures of $(NO_2)_3^+$, which is the smallest size of the $(NO_2)_n^+$ cluster ions, we have performed electronic structure calculations of $(NO_2)_3^+$ adopting the DFT/B3LYP method with the aug-cc-pVQZ basis set as implemented in Gaussian16.[2] We have found that there are two stable isomers, in which two NO_2 form a planar structure and one linear-shaped NO_2^+ is attached to the planar neutral moiety so that the O-N-O bond axis is perpendicular to the plane formed by $(NO_2)_2$. To investigate the energy barrier between these two stable isomers and the effect of the orientation of the NO_2^+ moiety with respect to the plane of the planar $(NO_2)_2$ moiety, we calculated using the 6-31G(d) basis set the total energy of the cluster ion as a function of the angle formed by the N-N axis of $(NO_2)_2$ and a line connecting the N atom of NO_2^+ and one of the N atom of $(NO_2)_2$. It is found that, at the barrier between the two minima, the configuration in which the O-N-O axis of the NO_2^+ moiety is on the $(NO_2)_2$ plane is lower in energy by ~0.05 eV than the configuration in which the O-N-O axis of the NO_2^+ moiety is perpendicular to the $(NO_2)_2$ plane, indicating that the isomerization between the two isomers in $(NO_2)_3^+$ accompanies the internal rotation of the linear NO_2^+ moiety with respect to the planar moiety of $(NO_2)_2$.

1) N. Washida, H. Shinohara, U. Nagashima and N. Nishi, *Chem. Phys. Lett*. **1985**, 121, 3, 223.
2) Gaussian 16, Revision B.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2016.