THE VIBRATIONAL ASSIGNMENT OF NO_3 IN THE GROUND ELECTRONIC STATE

EIZI HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa 240-0193, Japan*; KENTAROU KAWAGUCHI, *Department of Chemistry, Okayama University, Tsushima-naka 3-1-1, Okayama 700-8530, Japan*; TAKASHI ISHIWATA, *Department of Information Machines and Interfaces, Faculty of Information Sciences, Hiroshima City University, Ozukahigashi, Asaminami, Hiroshima 731-3194, Japan*; IKUZO TANAKA, *Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro, Tokyo 152-8550, Japan*.

We have previously analyzed a band of the NO_3 radical observed at 1492$cm^{-1}$and have established that the band was of E type, thus being assigned to the degenerate N-O stretching, ν_3 [a]. We have explained several anomalies noticed in the band in terms of a vibronic interaction model [b]. Stanton [c] recently proposed an alternative assignment $\nu_1 + \nu_4$ for this band, primarily based on an *ab initio* calculated potential. In order to establish the vibrational assignment of the band, we applied the vibronic interaction modelc to the $^{14}NO_3$-$^{15}NO_3$ isotope shift and calculated it to be 16 cm^{-1}in reasonable agreement with the observed value of 20 cm^{-1}[d] when the band is ν_3, whereas we obtained a very small value (about 1 cm^{-1}or less) for Stanton's assignment, at variance with the observed data. We have also scanned the region from 700 up to 1400 $cm^{-1}$to detect the ν_3 band predicted by Stanton at 994 cm^{-1}[e], by using a Fourier transform spectrometer. Although some part of this region was covered by strong absorption of the precursor HNO_3, we confirmed that there were no bands observed between 925 and 1277 cm^{-1}that were more than 1/10 as intense as the 1492 cm^{-1}band.

[a] T. Ishiwata *etal*., J. Chem. Phys. 82, 2196 (1985), K. Kawaguchi *etal*., J. Chem. Phys. 93, 951 (1990).
[b] E. Hirota *etal*., J. Chem. Phys. 95, 771 (1991).
[c] F. Stanton, J. Chem. Phys. 126, 134309 (2007).
[d] T. Ishiwata *etal*., J. Chem. Phys. 82, 2196 (1985).
[e] F. Stanton, J. Chem. Phys. 126, 134309 (2007).