



## Experimental determination of photo-dissociative isotopic fractionation of nitrate

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$\text{NO}_3^-$  is a reactive species formed at the end of the oxidation chain involving the atmospheric nitrogen compounds. The concentration and isotopic composition of various nitrate compounds can give important clues regarding the oxidative capacity of the atmosphere. However, nitrate can dissociate easily by UV photons below 350 nm which can cause decrease in concentration as well as changes in its isotopic composition since the absorption cross sections ( $\sigma$ ) of heavier (and rare) isotopic species are less than that of the (dominant)  $^{14}\text{N}^{16}\text{O}_3^-$  species in 300–340 nm range due to lowering of zero point energy (ZPE). Despite its importance, no direct measurements of  $\sigma$  for singly substituted isotopologues of nitrate have been reported so far. The present work reports data from our research in this regard.

Commercially available sodium nitrate was used for preparation of the  $^{14}\text{N}^{16}\text{O}_3^-$  and  $^{15}\text{N}^{16}\text{O}_3^-$  species. Two nominal 0.1 molar solutions were made with  $^{15}\text{N} : ^{14}\text{N}$  abundances of 0.37 : 99.63 (normal abundance) and 98.0 : 2.0 (strongly enriched in  $^{15}\text{N}$ ) and absorption spectra were taken by using a Perkin Elmer Vis–UV spectrophotometer in the range of 260–360 nm with a resolution of 1 nm. For determining the absolute cross section ratio, the two spectra were normalized through the molar concentrations. This normalization was checked by determining the area of  $\sigma$  versus energy by numerical integration with appropriately chosen lower and upper limits of wavelength. The good agreement between the two methods of normalization shows that coordinate dependence of the Transition Dipole Moment Surface is weak in the Franck–Condon region.

For preparing the heavy ( $^{14}\text{N}^{18}\text{O}^{16}\text{O}_2^-$ ) and light ( $^{14}\text{N}^{16}\text{O}_3^-$ ) oxygen isotopic nitrate species we used the following method: 6 ml of Sodium Nitrite solution at nominal 0.1 molar concentration ( $6 \times 10^{-4}$  mole) was made to react with ozone prepared from normal tank oxygen ( $^{16}\text{O} : ^{17}\text{O} : ^{18}\text{O} = 99.76 : 0.04 : 0.20$ ) and also from  $^{18}\text{O}$ -enriched oxygen ( $^{18}\text{O} \sim 99\%$ ). This reaction converts nitrite to nitrate via oxygen atom transfer from the terminal position of the ozone molecule. Completeness of the conversion was ensured by adding ozone in stoichiometric excess (about  $1.3 \times 10^{-3}$  mole). We therefore obtain nitrate with all three atoms being dominantly  $^{16}\text{O}$  in one case (about 99.8%) and two  $^{16}\text{O}$  plus one  $^{18}\text{O}$  in the other. The  $\sigma$  values were also recorded for the two commercially available sodium nitrate samples. The two cross section ratios,  $\sigma(^{15}\text{N}^{16}\text{O}_3^-)/\sigma(^{14}\text{N}^{16}\text{O}_3^-)$  and  $\sigma(^{14}\text{N}^{18}\text{O}^{16}\text{O}_2^-)/\sigma(^{14}\text{N}^{16}\text{O}_3^-)$  show variations from 0.95 to 1.01 in the relevant actinic zone resulting in a net decrease in the heavy  $\text{NO}_2$  species (product of photodissociation) and corresponding isotopic increase in the light over nitrate. However, the deviation from unity is more pronounced for the  $^{15}\text{N}^{16}\text{O}_3^-$  species than for the  $^{14}\text{N}^{18}\text{O}^{16}\text{O}_2^-$  species.

The fractionation factor  $\alpha$  is given by the ratio of the photodissociation rates  $J : \alpha = J'/J = \int F(\lambda) \times \sigma'(\lambda) d\lambda / \int F(\lambda) \times \sigma(\lambda) d\lambda$  where  $\lambda$  denotes the actinic flux and  $\sigma(\lambda)$  denotes the absorption cross section and prime denotes the heavier species. Using typical actinic flux for Antarctic Dome C station, the calculated enrichment factor,  $\epsilon$  ( $= (\alpha - 1) \times 1000$ ) for the two heavy isotope ratios are  $\sim -24 \pm 3\%$  for  $^{15}\text{N}^{16}\text{O}_3^-$  and  $\sim -12 \pm 5\%$  for  $^{14}\text{N}^{18}\text{O}^{16}\text{O}_2^-$ .

The shape of  $\sigma$  can be described by a four parameter analytic model which shows that the dominant effect causing fractionation is the decrease of the ZPE for heavy isotope substitution. However, the difference in enrichment between  $^{15}\text{N}$  and  $^{18}\text{O}$  substitutions cannot be predicted solely by variations in ZPE.