

Dispersed Fluorescence Spectroscopy of Jet Cooled NO₃ Radicals

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The nitrate free radical, NO₃, is one of the simple nitrogen oxides and important intermediates in atmospheric chemistry. In this investigation, we have generated NO₃ free radical in supersonic free jet expansion, and observed laser induced fluorescence (LIF) of the $\tilde{B}^2E' - \tilde{X}^2A_2'$ electronic transition. We have measured the LIF dispersed fluorescence (DF) spectra from the single vibronic levels (SVL) of the ¹⁴NO₃ and ¹⁵NO₃ isotopomers. The fluorescent levels of the spectra, i.e. the SVLs, are the 0+0, 0+770, 0+948, 0+1440, and 0+1637 cm⁻¹ and the 0+0, 0+777, 0+925, 0+1435, and 0+1660 cm⁻¹ bands for ¹⁴NO₃ and ¹⁵NO₃, respectively. (Since the widths of the vibronic bands are much wider than those of the molecules without Douglas effect, the band positions do not express the vibronic level energy, but the peak of the bands for the measurement of the SVL DF spectra). In the LIF DF spectra, a strong correlation is observed between the two isotopomers (of course, within the isotope shifts). In the LIF DF spectra with our standard resolution (~7 cm⁻¹ in FWHM) obtained by the excitation of the 0+0 cm⁻¹ band, the 1053 cm⁻¹ band of ¹⁴NO₃ is observed as two bands, 1039 and 1053 cm⁻¹, with an intensity ratio of 4 : 5, respectively, for ¹⁵NO₃. Higher resolution measurements (~2 cm⁻¹ in FWHM) of the DF spectra show that the 1053 cm⁻¹ band of ¹⁴NO₃ is also observed as two bands at 1051 and 1056 cm⁻¹ with an intensity ratio of 5 : 3, respectively. The stronger band in spectrum of each species, i.e. the 1051 and 1053 cm⁻¹ band for ¹⁴NO₃ and ¹⁵NO₃, respectively, is attributed to be the ν_1 (a_1') fundamental, because of its little isotope shift, though the isotope shift shows inverse behavior with the usual. There are three possibilities for another band at 1055 and 1038 cm⁻¹ for ¹⁴NO₃ and ¹⁵NO₃, respectively, and with the isotope shift of 17 cm⁻¹: (1) the ν_3 (e') fundamental band¹, (2) the $\nu_2 + \nu_4$ (a_2'' and e' , respectively) combination band, and (3) the third over-tone, $3\nu_4$, band (a_1' , $l = 3$). If the dominant mechanism is (1), the ν_3 band should be observed in IR spectrum, but it has yet to be observed. If (2), the intensity must be stolen from the $\tilde{B}^2E' - \tilde{A}^2E''$ transition through the ν_2 mode, the considerable transition moment of which has been predicted². A simple consideration for the vibronic coupling³ between the \tilde{A}^2E'' and \tilde{X}^2A_2' states through the ν_2 mode may account for approximately 20 % of the combination band intensity to that of the ν_1 fundamental. If (3), it is unusual that the energy of the $3\nu_4$ a_1' level ($l = 3$) is 120 cm⁻¹ lower than the $3\nu_4$ e' level ($l = 1$), for the latter of which, the origin is reported to be 1173.629 and 1159.2456 cm⁻¹, for ¹⁴NO₃ and ¹⁵NO₃, respectively⁴ (the 14 cm⁻¹ isotope shift). It is revealed that the ν_4 vibrational mode of the \tilde{X}^2A_2' state has large an-harmonicity⁵, which is thought to be caused by vibronic coupling with the \tilde{B}^2E' electronic excited state through the ν_4 mode. While the e' level of $3\nu_4$ is affected by the coupling, it is expected to be negligible coupling for the a_1' level because of equivalence of $l = 3$ with $l = 0$, and to lie at its regular (without perturbation) position, ~1050 cm⁻¹ ($= 3 \times 350$ cm⁻¹). Thus, if the ν_4 vibronic coupling is possible, (3) can explain the inverse isotope shift of the ν_1 fundamental level and the isotope shifts of 17 and 14 cm⁻¹ for the $3\nu_4$ a_1' and e' levels, respectively; the ν_1 level is perturbed by the upper or lower a_1' level of $3\nu_4$ for ¹⁴NO₃ and ¹⁵NO₃, respectively, and the coupling is about 1 cm⁻¹.

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