DISPERSED FLUORESCENCE SPECTROSCOPY OF THE $\tilde{B}\ ^2E'$ – $\tilde{X}\ ^2A_2'$ TRANSITION OF JET COOLED $^{14}NO_3$ and $^{15}NO_3$

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We have generated NO_3 in supersonic free jet expansions and observed laser induced fluorescence (LIF) of the $\tilde{B}\ ^2E'$ – $\tilde{X}\ ^2A_2'$ transition. We have measured LIF excitation spectra and dispersed fluorescence (DF) spectra from the single vibronic levels (SVL's) of the $\tilde{B}\ ^2E'$ state of $^{14}NO_3$ and $^{15}NO_3$. The vibrational structure of the $\tilde{X}\ ^2A_2'$ state has been analyzed by comparing the vibrational structures of the DF spectra of the two isotopomers. The 1,053 cm^{-1} band of $^{14}NO_3$ is observed as two bands at 1,039 and 1,053 cm^{-1} with an intensity ratio of 4 : 5, respectively, for $^{15}NO_3$, which are observed in the DF spectra with our standard resolution ($\sim$ 7 cm^{-1} in FWHM). Higher resolution measurements ($\sim$ 2 cm^{-1} in FWHM) of the DF spectra show that the 1,053 cm^{-1} band of $^{14}NO_3$ is also observed as two bands at 1,051 and 1,056 cm^{-1} with an intensity ratio of 5 : 3, respectively. The 1,051 cm^{-1} band is attributed to be the ν_1 (a_1') fundamental, because of its little isotope shift. There are two possibilities for another band, the band at 1,056 and 1,038 cm^{-1} for $^{14}NO_3$ and $^{15}NO_3$, respectively; (1) the ν_3 (e') fundamental band[a], and (2) the $\nu_2 + \nu_4$ (a_2'' and e', respectively) combination band. If this is the case (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 predicted[b]. A simple consideration for the vibronic coupling[c] between the $\tilde{A}\ ^2E''$ and $\tilde{X}\ ^2A_2'$ states through the ν_2 mode can understand about 20 % of the combination band intensity to that of the ν_1 fundamental. The higher resolution measurements of the DF spectra also show that the 1,499 cm^{-1} band of $^{14}NO_3$ is much stronger than the 1,492 cm^{-1} band in the electronic spectrum, while the latter is the strongest band in the IR absorption spectrum[d].

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