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 $\nu_3$ ($a_{1}'$) 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 $\nu_3$ ($e'$) fundamental band$^a$, and (2) the $\nu_2 + \nu_4$ ($a''_2$ and $e'$, respectively) combination band. If this is the case (1), the $\nu_3$ band should be observed in IR spectrum, but it has yet to be observed. If (2), the intensity must be stolen from the $\tilde{B}^2E' - A^2E''$ transition through the $\nu_2$ mode, the considerable transition moment of which has been predicted$^b$. A simple consideration for the vibronic coupling$^c$ between the $A^2E''$ and $\tilde{X}^2A'_2$ states through the $\nu_2$ mode can understand about 20% of the combination band intensity to that of the $\nu_3$ 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$^d$.