VIBRONIC STRUCTURE OF THE $\tilde{X}\ ^2A_2'$ STATE OF NO_3

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We have measured dispersed fluorescence (DF) spectra from the single vibronic levels (SVL's) of the $\tilde{B}\ ^2E'$ state of jet cooled $^{14}NO_3$ and $^{15}NO_3$, and found a new vibronic band around the ν_1 fundamental[b]. This new band has two characteristics; (1) inverse isotope shift, and (2) unexpectedly strong intensity, i.e. comparable with that of the ν_1 fundamental. We concluded on the basis of the isotope effect that the terminated (lower) vibrational level of the new vibronic band should have vibrationally a_1' symmetry, and assigned to the third over-tone of the ν_4 asymmetric (e') mode, $3\nu_4$ (a_1'). We also assigned a weaker band at about 160 cm^{-1} above the new band to one terminated to $3\nu_4$ (a_2'). The $3\nu_4$ (a_1') and (a_2') levels are ones with $l = \pm 3$. Hirota proposed new vibronic coupling mechanism[c] which suggests that degenerate vibrational modes can induce electronic orbital angular momentum (L) even in non-degenerate electronic states. We interpret this as a sort of break-down of the Born-Oppenheimer approximation, and think that $\pm l$ induces $\mp\bar{\Lambda}$, where $\bar{\Lambda}$ expresses the pseudo-L; for the present system, one of the components of the third over-tone level, $|\Lambda = 0; v_4 = 3, l = +3\rangle$, can have contributions of $|\bar{\Lambda} = -1; v_4 = 3, l = +2\rangle$ and $|-2; 3, +1\rangle$. Under this interpretation, it is expected that there is sixth-order vibronic coupling, $(q_+^3 Q_-^3 + q_-^3 Q_+^3)$, between $|0; 3, +3\rangle$ and $|0; 3, -3\rangle$. The sixth-order coupling is weaker than the Renner-Teller term (the fourth-order term, $(q_+^2 Q_-^2 + q_-^2 Q_+^2)$), but stronger than the eighth-order term, $(q_+^4 Q_-^4 + q_-^4 Q_+^4)$. It is well known in linear molecules that the former shows huge separation, comparable with vibrational frequency, among the vibronic levels of Π electronic states, and the latter shows considerable splitting, $\sim$10 cm^{-1}, at Δ electronic states. Consequently, the $\sim$160 cm^{-1} splitting at v_4 = 3 is attributed to the sixth-order interaction. The relatively strong intensity for the band to $3\nu_4$ (a_1') can be interpreted as a part of the huge 0-0 band intensity, because the $3\nu_4$ (a_1') level, $|0; 3, \pm 3\rangle$, can connect with the vibrationless level, $|0; 0, 0\rangle$. $3\nu_4$ (a_1') has two-fold intensity because of the vibrational wavefunction, $|0; 3, +3\rangle + |0; 3, -3\rangle$, while negligible intensity is expected for $3\nu_4$ (a_2') with $|0; 3, +3\rangle - |0; 3, -3\rangle$ due to the cancellation. To confirm these interpretations, experiments on rotationally resolved spectra are underway.

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[b] M. Fukushima and T. Ishiwata, paper WJ03, ISMS2013, and paper MI17, ISMS2014.

[c] E. Hirota, $J.Mol.Spectrosc.$, in press.