Vibronic Coupling in the $\tilde{X}\ {}^2A_2'$ state of NO_3

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For the vibrational structure of the $\tilde{X}\ {}^2A_2'$ state of NO_3, two assignments are proposed; a traditional assignment and one proposed by Stanton [1]. The major difference is the position of the ν_3 fundamental, at 1492 and ~1000 cm^{-1}, respectively. To solve this problem, we have measured dispersed fluorescence (DF) spectrum from the single vibronic levels (SVL's) of the $\tilde{B}$ state of jet cooled NO_3, for both isotopomers, $^{14}NO_3$ and $^{15}NO_3$ [2]. The spectrum from the vibration-less level consists of three regions; (I) regions around 1050 and 1500 cm^{-1}, (II) the region below 1850 cm^{-1} except (I), and (III) the region above 1850 cm^{-1}. Region II displays relatively regular vibrational structure including ν_1 fundamental and ν_4 progressions, 4^0_n, n = 0, 1, 2, 3, and $1^0_1 4^0_n$, n = 0, 1, 2. Region III possesses congested structure with levels thought to be heavily mixed difficult to vibrationally characterize. In this paper, we will focus the vibrational structure of the region I and the 2nd over-tone region of ν_1, ~2000 cm^{-1}, in region III, and discuss vibronic coupling in the $\tilde{X}\ {}^2A_2'$ state.

First of all, three important findings are described. (1) We have found a new vibronic band very close to the ν_1 fundamental in region I [2], and thus two relatively intense vibronic bands are observed in the ν_1 fundamental region, ~1050 cm^{-1}, on the DF spectrum. In contrast, no bands have been detected in this region of the IR spectrum [3]. (2) In the 1500 cm^{-1} region of (I), only one intense band at 1500 cm^{-1} is observed on DF, while two bands at 1492 and 1499 cm^{-1}, which are *e*' and a_1' bands, respectively, are identified on IR hot bands [3]. (3) In the 2 ν_1 region, two bands, at 2010 and 2118 cm^{-1}, are observed on DF, and both are attributed to be a_1', because they have not been observed on IR [4]. The two bands show regular isotope shift [2]. Assuming Stanton's assignment, the levels at 1055 cm^{-1} (observed only on DF) and 1492 cm^{-1} (observed only on IR) will be attributed to the *e*' bands of the ν_3 fundamental and $\nu_3 + \nu_4$ combination levels, respectively, and his calculated DF spectrum quite nicely reproduces the observed [1]. However, this calculated DF spectrum does not match the observed DF spectrum. If the new band at 1055 cm^{-1} is labeled an *e*' band of the ν_3 fundamental, then the *e*' band of the combination, i.e. the 1492 cm^{-1} band, should be observed even in DF, but it isn't, while the a_1' band at 1500 cm^{-1} was remarkably observed in both DF and IR. In addition to this mismatch at ~1500 cm^{-1}, it is unusual for IR that no *e'* bands in region I have been observed; e.g. the ν_3 fundamental, expected to lie at 1055 cm^{-1}, should be observed in the IR spectrum, because the *e'* band of the combination at 1492 cm^{-1} is observed as the strongest band. Generally, a_1' bands are preferentially observed in DF. Thus we think that the two intense bands at 1055 and

1499 cm^{-1} on DF are both attributed to a_1'. The inverse isotope shift of the ν_1 fundamental lying close to the former [2] is easily understandable, and the major component of the latter is thought to be the 2nd over-tone of ν_2 (this is an out-of-plane umbrella mode, and the fundamental is at 762 cm^{-1} [3]), in which a favorable Franck-Condon factor is expected. This raises the question, what is the 1055 cm^{-1} a_1' band ?

We assign the 1055 cm^{-1} band to the 3rd over-tone of the ν_4 asymmetric (e') mode, 3 ν_4 (a_1'). We also assigned a weaker band at about 160 cm^{-1} above the new band to one with a final vibrational level of 3 ν_4 (a_2'). The 3 ν_4 (a_1') and (a_2') levels are ones with l = ±3. On the basis of experimental evidence of the strong correlation of the spin-orbit constant upon the ν_4 vibrational level, Hirota proposed a new vibronic coupling mechanism which suggests degenerate vibrational modes induce electronic orbital angular momentum even in non-degenerate electronic states and $K = \Lambda + l$ (this is written as $\overline{\Lambda} = \Lambda + l$ in [5]) should be conserved, where Λ is the induced Λ [5]. According to this, one of the components of the 3rd over-tone level, $| K = +3 \,;\, \Lambda = 0 \,;\, v_4 = 3 \,,\, l = +3 \rangle$, can have contributions of three components, $| +3 \,;\, +1 \,;\, 3 \,,\, +2 \rangle$, $| +3 \,;\, +2 \,;\, 3 \,,\, +1 \rangle$, and $| +3 \,;\, +3 \,;\, 3 \,,\, 0 \rangle$. The counter pair of the state, $| -3 \,;\, 0 \,;\, 3, -3 \rangle$, has contributions of $| -3 \,;\, -1 \,;\, 3, -2 \rangle$, $| -3 \,;\, -2 \,;\, 3 \,,\, -1 \rangle$, and $| -3 \,;\, -3 \,;\, 3 \,,\, 0 \rangle$. Accordingly, it is expected that there are sixth-order vibronic couplings, $({q_+}^2 {Q_+}^4 + {q_-}^2 {Q_-}^4)$ and $({q_+}^4 {Q_+}^2 + {q_-}^4 {Q_-}^2)$, for the 1st and 2nd components, respectively, among the three between the two 3 ν_4 components with l = ±3, $| +3 \,;\, 0 \,;\, 3, +3 \rangle$ and $| -3 \,;\, 0 \,;\, 3, -3 \rangle$. The two 6th order couplings above can be interpreted as 2nd order coupling of the 3rd order couplings, $(q_+ Q_+^2 + q_- Q_-^2)^2$: Hirota-type [6] and $({q_+}^2 Q_+ + {q_-}^2 Q_-)^2$: dynamical-Jahn-Teller-type, respectively. In the case of Renner-Teller interaction which is a typical of vibronic interactions, the 6th order couplings are weaker than the Renner-Teller term (the 4th order term, $({q_+}^2 {Q_-}^2 + {q_-}^2 {Q_+}^2)$), but stronger than the 8th order term, $({q_+}^4 {Q_-}^4 + {q_-}^4 {Q_+}^4)$. It is well known in linear molecules that the former, the 4th order term, shows huge splitting, comparable with vibrational frequency, among the vibronic levels of Π electronic states, and the latter, the 8th order term, shows considerable separation, ~10 cm^{-1}, for Δ electronic states. Consequently, the ~160 cm^{-1} splitting at v_4 = 3 is attributed to the 6th order interaction. The relatively strong intensity for the band to 3 ν_4 (a_1') can be interpreted as part of the huge 0-0 band intensity, because the 3 ν_4 (a_1') level, $| \pm 3 \,;\, 0 \,;\, 3 \,,\, \pm 3 \rangle$, can connect with the vibration-less level, $| \; 0 \,;\, 0 \,;\, 0 \,, 0 \rangle$, through the Hirota- and dynamical-Jahn-Teller-types coupling above. 3 ν_4 (a_1') has two-fold intensity because of the vibrational wavefunction, $| +3;\, 0 \,;\, 3, +3 \rangle + | -3;\, 0 \,;\, 3, -3 \rangle$, while negligible intensity is expected for 3 ν_4 (a_2') with $| +3;\, 0 \,;\, 3, +3 \rangle - | -3;\, 0 \,;\, 3, -3 \rangle$ due to cancellation.

[1] J. F. Stanton, *J. Chem. Phys.* 126, 134309 (2007) and 69th ISMS, paper MI16.
[2] M. Fukushima and T. Ishiwata, 68th ISMS, paper WJ03.
[3] K. Kawaguchi *et al.*, *J. Phys. Chem. A* 117, 13732 (2013).
[4] T. Ishiwata *et al.*, *J. Phys. Chem. A* 82, 980 (2010). [5] E. Hirota, *J. Mol. Spectrosco.* 310, 99 (2015).
[6] E. Hirota, K. Kawaguchi, T. Ishiwata, and I. Tanaka, *J. Chem. Phys.* 95, 771 (1991).