SVL Dispersed Fluorescence Spectra of NO_3
— Interpretation of the ν_4 progressions —

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We have generated NO_3 in supersonic free jet expansions and observed the laser induced fluorescence (LIF) spectrum of the $\tilde{B}\ ^2E' - \tilde{X}\ ^2A_2'$ electronic transition. We have measured dispersed fluorescence (DF) spectra from the single vibronic levels (SVL's) of the $\tilde{B}$ state of $^{14}NO_3$ and $^{15}NO_3$ [1]. A noticeable feature of both spectra from the vibration-less level is the appearance of ν_4 progressions (the ν_4 mode is a degenerate bending vibrational mode); in the spectra, the progressions, 4^0_n, n = 0, 1, 2, 3, and $1^0_1 4^0_n$, n = 0, 1, 2, exhibit decreasing intensities with increasing quantum number. In this paper, we will discuss the appearance of the ν_4 progressions.

(1) Discussion of the ν_4 progressions focusing only those in the fluorescence spectrum

To understand the progression, we can simply follow the discussion for transitions between degenerate and non-degenerate electronic states described in Herzberg's book [2]. In this book, the progressions to even vibrational levels with a_1 symmetry and with l = 0 are only allowed, when the degenerate state has no Jahn-Teller vibronic coupling. In contrast, regular progressions, i.e. bands to all of the levels, are allowed, when it has the coupling. Under the linear Jahn-Teller coupling regime, progression with regular intensity distribution, similar to that for non-degenerate vibrational modes, reflecting Franck-Condon factors, is expected [3]. In the present NO_3 case, if the $\tilde{B}\ ^2E'$ state will affect the linear Jahn-Teller coupling, the fluorescence to the $\tilde{X}\ ^2A_2'$ state should display a regular progression. But there is another spectrum displaying the vibrational structure of the $\tilde{X}\ ^2A_2'$ state of NO_3, i.e. photo-electron (PE) spectrum, and it will be realized that this simple consideration cannot be acceptable, as shown in the next.

(2) Discussion of the ν_4 progression focusing on the photo-electron spectrum

Neumark measured the PE spectrum of NO_3^-, and the ν_4 progression is observed in the spectrum for the $\tilde{X}\ ^1A_1'$ state of NO_3 [4]. Because the PE spectrum is a transition between non-degenerate electronic states, i.e. that from the $\tilde{X}\ ^1A_1'$ state of the anion to the $\tilde{X}\ ^2A_2'$ state of the radical with a PE, vibronic coupling cannot be expected in both states. It was thus proposed that Herzberg-Teller (H-T) vibronic coupling of the $\tilde{X}\ ^2A_2'$ state with the $\tilde{B}\ ^2E'$ state induces the progression, i.e. the $\tilde{X}$ state is mixed with $\tilde{B}$, where Hamiltonian of H-T has selection rule, $\Delta\Lambda = \pm 1,\ \Delta l = \mp 1$, and it is thus an inter-state coupling (This coupling may be called as pseudo-Jahn-Teller interaction, but here we describe this as H-T to clarify the coupling Hamiltonian, H_{HT}). Under the H-T approximation, the transition moment, $\mu_{v-\text{ion}}$, to a vibronic level, v, is expressed as

$$\mu_{v-\text{ion}} = \langle\, \text{radical}\,;\tilde{X}\ ^2A_2'\ + \text{photo electron}\,\big|\,\mu_e\,\big|\,\text{ion}\,;\ \tilde{X}\ ^1A_1'\,\rangle\langle\chi_v|\chi_{\text{ion}}\rangle$$

$$+ \frac{\left\langle \text{radical+pe} \left| {}^{d}\!/_{dQ_v} V_e \right| \text{ion} \right\rangle}{\Delta E} \left\langle \text{radical} ; \tilde{B}\ {}^2E' + \text{photo electron} \left| \mu_e \right| \text{ion} ; \tilde{X}\ {}^1A_1' \right\rangle \left\langle \chi_v | Q_v | \chi_{\text{ion}} \right\rangle .$$

The transition moment to the even levels has the 1st term as the major component, because of the energy denominator of the second term. In contrast, the transition moment to odd levels has only the 2nd term, because the 1st term becomes 0 due to $\Delta l \neq 0$ for the Franck-Condon over-lap, $\langle \chi_v | \chi_{\text{ion}} \rangle$, employing mechanism similar to intensity stealing (borrowing). This means that the vibronic bands to the even and odd levels, which are a_1' and e' symmetries, respectively, have different electronic transition moments. Initiated by this discussion, Stanton carried out a computational study, and reproduced not only the PE, but also DF spectrum [5]. Although the calculated spectra quite nicely reproduce the observed spectra, it is suggested that the vibronic coupling is too strong not only on the $\tilde{X}\ {}^2A_2'$ state [6], but also on $\tilde{A}\ {}^2E''$ [7].

In addition to this over-estimation of the coupling, when we applied the H-T coupling to the understand the ν_4 progressions on the fluorescence spectrum, a curious term, $\left\langle \tilde{B}\ {}^2E' \left| \mu_e \right| \tilde{B}\ {}^2E' \right\rangle$, is noted, which gives the transition intensity for the bands to the odd levels. Thus we present our mechanism here.

(3) Proposed mechanism

Hirota proposed a new mechanism which suggests that degenerate vibrational modes can induce electronic orbital angular momentum even in non-degenerate electronic states, and $K = \Lambda + l$ (this is written as $\bar{\Lambda} = \Lambda + l$ in [6]) should be conserved, where Λ is the induced Λ [6]. We interpret this to mean that degenerate vibrations are strongly coupled with electron motion, and that the vibronic wave-function cannot be separated, $|K; \Lambda; l\rangle \neq |\Lambda\rangle|l\rangle$. When we accept the vibronic coupling in the $\tilde{X}\ {}^2A_2'$ and $\tilde{B}\ {}^2E'$ states, the progressions are naturally interpreted, because all members of the progressions are vibronically allowed. This is effective not only for the DF spectrum, but also PE.

(4) Why does the vibronic coupling occur in the non-degenerate $\tilde{X}\ {}^2A_2'$ state ?

It is thought that one reason for the strong coupling of the degenerate vibration and non-degenerate electron motion in the state is nature of the molecular orbital (MO) of the un-paired electron, i.e. under a simple picture of the MO structure, the MO, $1a_2'$, of the state is a non-bonding one and consists only of $2p$s of three O atoms [8], and the contribution of the center N atom is negligible, as displayed in [9]. It is thus thought that, under the situation, the MO easily follows the vibrational motion (motions of three O's).

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