

2C-R4WM SPECTROSCOPY OF JET COOLED NO₃ (II)

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We have generated NO₃ in a supersonic free jet expansion, and observed laser induced fluorescence (LIF) and two-color resonant four-wave mixing (2C-R4WM) signals. We have measured dispersed fluorescence (DF) spectra from single vibronic levels. Among the vibrational levels observed in the DF spectrum from the vibration-less level, the ν_1 and ν_3 fundamental regions (~ 1050 and ~ 1500 cm⁻¹ regions, respectively) are now active for discussion, and thus we have tried to measure the rotationally resolved 2C-R4WM spectra^a. The 2C-R4WM spectrum of the ν_3 fundamental region is consistent with a previous infra-red investigation^b, and that of ν_1 leads to the identification of the $K = 0$ and $N = 1$ level of the ν_1 fundamental for the first time. We have found an additional level near ν_1 ^c, and the 2C-R4WM spectrum of the level shows two rotational transitions separated by 0.27 cm⁻¹. Although the 0.27 cm⁻¹ separation is about 10 times larger than the spin splitting, ~ 0.025 cm⁻¹, of the $K = 0$ and $N = 1$ levels at the other a'_l levels with $l = 0$, such as vibration-less and ν_1 (the latter value of which, 0.025 cm⁻¹, cannot be resolved under our instrumental resolution), the two transitions are thought to correspond to those terminating to spin sub-levels, $J = 0.5$ and $J = 1.5$, at the present. We have assigned the additional level to $3\nu_4$ (a'_l) with $l = \pm 3$. For Σ vibronic levels with $K = 0$, such as $v_d = 1$ and $l = 1$, of a $^2\Pi$ electronic state, it is well known that $^2\Sigma^{(+)}$ and $^2\Sigma^{(-)}$ vibronic levels have relatively large Ω - or ρ -type doubling due to non-zero Λ , in spite of the Σ vibronic levels^d. It is thought that the unexpectedly large spin splitting, 0.27 cm⁻¹, is induced by spin-vibration interaction, which has been discussed for degenerate vibronic levels of non-degenerate electronic states, $^2\Sigma$ and $^3\Sigma$, of linear polyatomic molecules^e.

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