TWO-PHOTON TRANSITIONS IN THE LASER INDUCED FLUORESCENCE OF NO_3 BY FUKUSHIMA

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Recently, Fukushima reported laser-induced fluorescence of the $\tilde{B}^2E'$ - $\tilde{X}^2A'_2$ transition from the vibrationless $\tilde{B}^2E'$ excited state of jet cooled $^{14}NO_3$ and $^{15}NO_3$ in which two beautiful series of ν_4 progressions in the ground $X^2A'_2$ state have been identified.[a] One of the progressions corresponds to transitions with vibrational symmetry a_1' - a_1' while the other with a_1' - e'. The former is the ordinary single-photon spontaneous emission given in Eq.(II,11) of Herzberg Vol.III, while the latter is not discussed in ordinary textbook of spectroscopy. Here I propose that the latter is due to Raman-type laser stimulated two-photon processes that were commonly observed around 1970.[b,c]

Contrary to the previous assignments which invoke vibronic mixing between the $\tilde{B}^2E'$ and $\tilde{X}^2A'_2$ states, the 2-photon assignment leaves the vibrational angular momentum l_4 in the ground $\tilde{X}^2A'_2$ state a good quantum number except for the $\Delta l = 3$ mixing. Therefore the l_4 assignment and the vibrational structure are extremely simple as reported in the Fukushima paper. The calculation using the Kramers-Heisenberg formula indicates that the laser power density indicates sufficiently high to cause the two-photon process.

The perfectly normal ν_4 progression suggests strongly that the ν_3 progression is also normal. This suggests that the so-called "Assignment I" in which the intensity of the ν_3 fundamental band is higher than that of the $\nu_3 + \nu_4$ combination band is more reasonable than the "Assignment II" in which a theoretical calculation gives the ν_3 band weaker than the $\nu_3 + \nu_4$ band by a factor of 60[d] and an experimental observation by $\sim$ 2000.[e]

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[a] Fukushima, M. 2022, J. Mol. Spectrosc. 387, 111646

[b] Freund, S.M., Oka, T. 1976, Phys. Rev. A. 13, 2178

[c] Oka, T. 1977, Frontiers in Laser Spectroscopy, II (Proceedings, Summer School of Theoretical Physics, Les Houches), R. Balian, S. Haroche and S. Lieberman, eds., North-Holland, Amsterdam, pp. 531–569

[d] Stanton, J.F. 2009, Mol. Phys. 107, 1059

[e] Kawaguchi, K., Tang, J., Akikusa, N. 2021, Chem. Phys. Lett. 765, 138365