VIBRATIONAL ANALYSIS OF DF SPECTRUM OF THE NO $_3$ \tilde{B} $^2E'$ – $^2A'_2$ SYSTEM (II): COMBINED ANALYSIS WITH CRYO-SEVI PE SPECTRUM OF NO $_3^-$

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We are currently studying the \tilde{B} $^2E'$ – \tilde{X} $^2A'_2$ system of jet cooled NO₃ via laser induced fluorescence (LIF) spectroscopy. The dispersed fluorescence (DF) spectrum from the vibrationless level of the upper electronic state suggests the existence of two closely lying vibrational levels in the ν_1 fundamental region, ~ 1050 cm^{-1a}. Recently, Babin et al. reported the high resolution photo-electron (PE) spectrum of NO₃ measured by a spectroscopic method, slow photo-electron velocity-map imaging of cryogenically cooled anion (cryo-SEVI)^b, but unfortunately, the cryo-SEVI PE spectrum does not resolve the two levels in the ν_1 fundamental region. In the report, it is also shown that the PE band intensities depend on the excess kinetic energy of PE by the photo-detachment light source. This dependence is also reported in their spectra measured by traditional PE spectroscopy^c. By combining results from these two methodologies, we have analyzed the excess energy dependence of the PE bands, and found that there are two components with different excess energy dependence in the ν_1 fundamental region. The two components can be attributed two vibrational levels, consistent with our DF results. The dependence of one of the two components corresponds to that of the vibrationless band (vibrationally a'_1), while the other does not agree with that of the ν_4 fundamental (e'), ~ 350 cm⁻¹.

^aM. Fukushima and T. Ishiwata, ISMS2013, paper WJ03 (2013).

^bM. Babin, J. A. DeVine, M. DeWitt, J. F. Stanton, and D. M. Neumark, J. Phys. Chem. Lett. 11, 395 (2019)

^cA. Weaver, D. W. Arnold, S. E. Bradforth, and D. M. Neumark, J. Phys. Chem. 94, 1740 (1991)