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EXPERIMENTAL EVIDENCE OF THE ν_3 MODE IN NO_3 VIA SLOW PHOTOELECTRON VELOCITY-MAP IMAGING OF COLD NO_3^-

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With five electronic states within 2 eV, the nitrate radical (NO_3) has a rich vibronic landscape for which photoelectron spectroscopy is an ideal probe. Here, we use slow photoelectron velocity map imaging of cryogenically cooled anions (cryo-SEVI), a high-resolution variant of anion photoelectron spectroscopy, to investigate the vibronic structure of the $\tilde{X}^2A_2'$ state of NO_3. Our cryo-SEVI spectra are in excellent agreement with Franck-Condon simulations produced using a three-state Köppel-Domke-Cederbaum (KDC) Hamiltonian constructed for the NO_3 radical. Together, the experimental and simulated spectra provide clear evidence that the ν_3 fundamental resides near 1060 cm^{-1}, resolving a long-standing controversy surrounding this vibrational fundamental. Further, the appearance of activity along the ν_4 mode in this cryogenically-cold system verifies its activity through a Herzberg-Teller interaction, rather than as a hot band as previously suggested.