HIGH-RESOLUTION, JET-COOLED INFRARED SPECTROSCOPY OF *TRANS*-FORMIC ACID: ANALYSIS OF ν_1 OH STRETCHING FUNDAMENTAL

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High-resolution infrared reduced-Doppler absorption spectra of jet-cooled gas phase *trans*-formic acid at $T_{rot} \approx$ 10.9(5) K are reported for the first time in the ν_1 OH stretching fundamental region, obtained by supersonically expanding *trans*-formic acid/Ar mixtures through a slit jet nozzle source. Four rovibrational bands are observed, with origins at 3570.493(5) (*a*/*b*-type), 3566.793(5) (*a*/*b*-type), 3560.032(9) (*b*-type), and 3534.6869(2) (*a*-type) cm^{-1}, respectively. Based on previous Raman jet spectroscopic work by Nejad and Sibert[a], these four bands have been assigned to ν_1, ν_2 + ν_7, ν_6 + $2\nu_7$ + $2\nu_9$ (tentatively by our work), and $2\nu_3$, respectively. Specifically, two of the three upper dark states $2^1 7^1$ (a′) and $6^1 7^2 9^2$ (a′) are close enough to the "bright" 1^1 (a′) state to facilitate strong anharmonic resonance interactions, resulting in intensity mixing into the two zero-order bands that would otherwise be "dark". Furthermore, our high-resolution spectral analysis reveals that there are local rotational crossings between zero-order 1^1 and $2^1 7^1$ states. This motivates the development of a 3 coupled state (1^1, $2^1 7^1$, and $6^1 7^2 9^2$) picture to aid in the spectral analysis, which is able to match all 3 observed band origins and relative band intensities, as well as indicate the necessity of multistate coupling. Though limited by the range of J and K_a levels ($J' \leq 9$ and $K'_a \leq 3$) populated at supersonic jet temperatures, this work offers the first precision spectroscopic analysis of *trans*-formic acid in the ν_1 OH stretching region, which should aid in the assignment of the more complete yet highly congested room temperature FTIR spectra[b].

[a] A. Nejad, E.L. Sibert III, The Raman jet spectrum of trans-formic acid and its deuterated isotopologs: Combining theory and experiment to extend the vibrational database, J. Chem. Phys. 154(6) (2021) 064301.

[b] D. Hurtmans, F. Herregodts, M. Herman, J. Liévin, A. Campargue, A. Garnache, A. Kachanov, Spectroscopic and ab initio investigation of the ν_{OH} overtone excitation in trans-formic acid, J. Chem. Phys. 113(4) (2000) 1535.