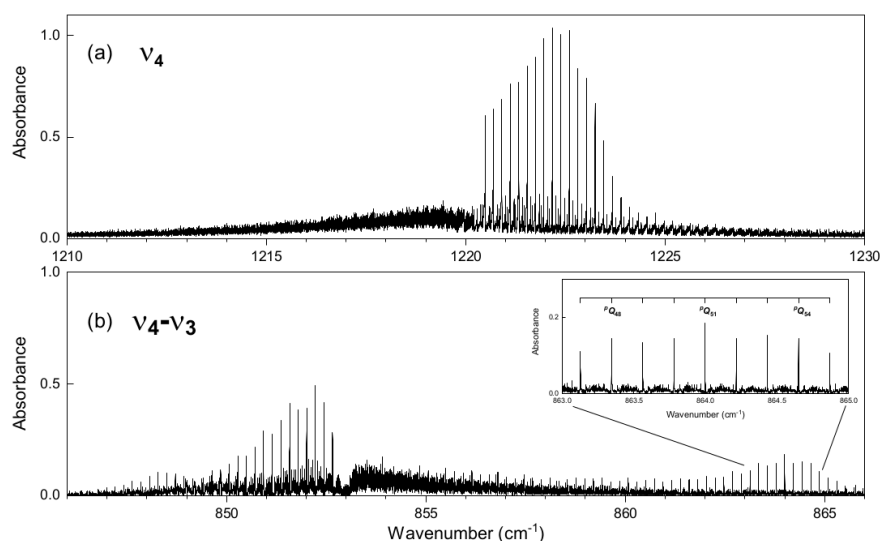


HIGH-RESOLUTION ROVIBRATIONAL SPECTROSCOPY OF $\text{CH}^{35}\text{Cl}_3$: CLUSTERING EFFECTS IN THE ν_4 AND $\nu_4 - \nu_3$ BANDS

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The $\nu_4 = 1$ fundamental vibration of $\text{CH}^{35}\text{Cl}_3$ (C-H bending, E symmetry) has been revisited at high-resolution. For this purpose, three FTIR spectra, recorded respectively in the regions of the ν_4 (1220 cm^{-1}), $\nu_4 - \nu_3$ (853 cm^{-1}), and ν_3 (367 cm^{-1}) bands were employed. Spectra were all recorded at the Synchrotron Soleil, at a resolution of 0.001 cm^{-1} but with various optical pathlengths (12, 24, and 84 meters, respectively), using a monoisotopic $\text{CH}^{35}\text{Cl}_3$ sample (99 % purity). As can be seen in the figure below, both the ν_4 and $\nu_4 - \nu_3$ bands show remarkable clustering effects, due to the smallness of some combinations of rovibrational parameters.



These clustering effects are sometimes source of misassignments, especially when the systematic use of the lower state combination difference as a checking is not possible. In the present work, the assignment checking has been done through fundamental and difference transitions sharing a common upper level. This procedure allowed us to systematically correct and extend the K -assignments of the ${}^rR_K(J)$ transitions in the ν_4 band, with respect to the previous high-resolution study¹. The least-squares fit, performed on more than 6900 transitions of the ν_4 and $\nu_4 - \nu_3$ bands ($0 \leq J \leq 100$ and $-75 \leq K \cdot \Delta K \leq 75$), combined with 800 IR (ν_3) and 1300 MMW ($\nu_3 = 1$) data, allowed to obtain an accurate description of the $\nu_4 = 1$ level (global standard deviation of 0.160 cm^{-1}).

¹R. Anttila, S. Alanko, V.-M. Horneman, *Mol. Phys.* **102** (2004) 1537-1542.