INTERACTIONS IN SYMMETRIC TOP MOLECULES BETWEEN VIBRATIONAL POLYADS: ROTATIONAL AND ROVIBRATIONAL SPECTROSCOPY OF LOW-LYING STATES OF PROPYNE

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A large body of very accurate (mostly 10–20 kHz) rotational transitions within the 10 μm tetrad of the strongly prolate symmetric rotor propyne, $H_3C–C{\equiv}CH$, had been recorded in order to analyze some weaker resonances.[a] The analysis, in particular for higher K transitions, indicated new problems: Interactions of members of the 10 μm tetrad ($v_5 = 1$, $v_9 = v_{10} = 1$, $v_{10} = 3$, and $v_8 = 1$) with those of the 15 μm dyad ($v_9 = 1$ and $v_{10} = 2$).

More than 300 rotational transitions within $v_{10} = 1$ ($E_{\rm vib}$ = 330.9 cm^{-1}) have been recorded with $J'' \leq 53$ and $-11 \leq K \cdot l_{10} \leq +16$ for a more systematic investigation into the lower excited vibrational states of propyne. Even the inclusion of many high order terms prevented the highest K transitions to be fit within experimental uncertainties, in particular those having $K \cdot l_{10} \leq 0$. Inclusion of ν_{10} IR transitions from a reanalysis of the spectrum that was used in the study of the 10 μm tetrad[a] confirmed these findings. It turned out that the first order energies of the $K \cdot l_{10}$ = –12 levels coincide to within 1 cm^{-1} with those of the overtone $v_{10} = 2$, K = 12 of the l_{10} = +2 substate. A weaker Coriolis interaction occurs between $v_{10} = 1$, $K \cdot l_{10}$ = –11 and $v_9 = 1$, $K \cdot l_9$ = +10.[b]

Meanwhile, the investigation of $v_{10} = 1$ has been completed, and those of $v_9 = 1$ and $v_{10} = 2$ have begun. Fermi-type interactions occur between the states $v_{10} = 2$ and 3 and between $v_9 = 1$ and $v_9 = v_{10} = 1$. Among the Coriolis resonances, the one between $v_{10} = 2$, l_{10} = –2 and $v_5 = 1$ permitted intervibrational transitions to be detected in the submillimeter region. These interactions are expected to improve A, D_K, etc. for v = 0. Selected details of our ongoing analyses will be presented. In addition, the relevance of these types of interactions for other symmetric top molecules will be discussed.

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[a] P. Pracna, G. Graner, J. Cosléou, J. Demaison, G. Wlodarczak, V.-M. Horneman, and M. Koivusaari, *J. Mol. Spectrosc.* **206,** (2001) 150–157; H. S. P. Müller, P. Pracna, *et al.*, unpublished

[b] H. S. P. Müller, P. Pracna, and V.-M. Horneman, *J. Mol. Spectrosc.* **216,** (2002) 397–407