ANALYSIS OF A AND E COMPONENTS OF THE ν_{21} TORSIONAL FUNDAMENTAL OF PROPENE AT 188 cm^{-1}

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The far infrared spectrum of propene, $\mathrm{CH_3-CH=CH_2}$, has been measured at 193.65 K with a resolution of 0.00096 cm^{-1}on the FIR beamline at the Canadian Light Source (CLS) synchrotron. The torsional fundamental band ν_{21} at 188 $\mathrm{cm}^{-1}$is quite complex because the coupling of the angular momenta of the overall rotation with the internal rotation of the $\mathrm{CH_3}$ group splits every rovibrational energy level (without internal rotation) into an A- and an E-component. As a result, every rovibrational transition splits into two or three components. To predict and assign the spectrum and to determine spectroscopic constants by the LS method, the ERHAM program [b] has been modified to use it for rovibrational spectra.

Initially, the spectroscopic constants for the ground state (GS) were fixed at the values determined by Craig et al.[c] from almost 900 microwave and millimeter-wave frequencies. This was good enough to begin the assignment of transitions of ν_{21} involving low K_a levels. However, for $K_a > 3$, the ratio of the standard deviation over the estimated experimental uncertainty increased with increasing K_a despite the introduction of additional tunneling parameters.

Only the inclusion of the internal rotation parameters ρ and β (which had been held constant with the GS constants) among the variable parameters brought the standard deviation down to an acceptable level. From then on, the transitions of ν_{21} were used simultaneously with all GS transitions (footnote b) to fit the parameters of two different effective internal rotation Hamiltonians (one each for the GS and ν_{21} levels) but with shared ρ and β. More than 6000 individual transitions (J up to 50, K_a up to 8) have been assigned so far for the ν_{21} band and preliminary constants have been obtained, among them an improved internal rotation barrier.

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[a] Deceased Sept. 21, 2021

[b] P. Groner, J. Chem Phys. (1997) 107, 4483; J. Mol. Spectrosc. (2012) 278, 52

[c] N. C. Craig et al., J. Mol. Spectrosc. (2016) 328, 1