MODELING OF THE FUNDAMENTAL RAMAN AND INFRARED CH STRETCHING SPECTRA OF CHD_2 PICOLINES

C. LAPOUGE, D. CAVAGNAT, *Laboratoire de Spectroscopie Moléculaire et Cristalline, URA 124, 351 crs de la Libération, 33405 Talence, FRANCE.*

The quasi-free internal rotation of the methyl group in the α, β and γ CHD_2 picolines leads to complex features observed in the Raman and infrared CH stretching spectra. A quantum theory has been developped to model these spectra, taking explicitely into account the coupling between the slow internal motion and the much faster CH stretching vibration.

In the ground vibrational state (v=0), the effective potential of internal rotation is calculated by adding to the methyl rotation potential energy, the variation of the zero point vibrational energy during the internal motion, determined by ab-initio.

In the CH stretching excited state, this effective potential is added to the CH stretching vibrational contribution, determined from the conformational dependence of the CH bond length.

The CH transitions between the effective potentials in the ground (v=0) and the first excited (v=1) CH stretching states are then calculated to reconstruct the fundamental Raman and IR spectra. The Raman intensities are determined from simple Franck-Condom factors, and the IR intensities are calculated from dipole moment derivatives determined by ab-initio. The so calculated spectra agree well with the experimental ones.