METHYL ROTOR INTRAMOLECULAR DYNAMICS OF GASEOUS NITROMETHANES NO_2CH_3 AND NO_2CH_2D

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The internal rotation of the methyl group in nitromethanes NO_2CH_3 and NO_2CH_2D are studied through the CH bond stretching overtones (Δv = 1 to 6). The spectra of the gaseous compounds are recorded by FTIR (Δv = 1 to 4) and by intracavity dye laser photoacoustic spectrometry (Δv = 5 and 6) at low resolution (0.5 to 2 cm^{-1}).

A quantum theory, assuming an anharmonic coupling of the ν(CH) mode with the methyl group internal rotation is used to analyse the experimental data (1). The used conformational dependent parameters are provided by ab-initio calculations (1,2). Theoretical calculations based on this model show that the effective internal motion potential in the high excited CH stretching states is essentially due to the vibrational energy contribution.

The Fermi resonance couplings with the combination states involving C-H stretch / CH_3 or CH_2D bending modes and C-H / C-D stretch modes are also considered and modelled. Contrary to what is observed in cyclopentene (3), these phenomena lead only to weak redistribution of the energy localized at the Δv = 3 vibrational state.

At high vibrational energy (Δv = 4 to 6), the major part of the features of the ν(CH) overtone spectra are determined by both methyl group internal rotation and vibration-rotation structure. The central band can be related to the average CH stretch during the methyl group rotation whereas the lower frequency peak can be assigned to the CH stretch of a C-H bond in a plane perpendicular to the molecular plane and the higher frequency one to the CH stretch of a C-H bond in the molecular plane.

At low vibrational energy (Δv = 1 and 2), the Coriolis coupling between the internal rotation and the two perpendicular stretching normal modes $\nu_a(CH_3)$ and $\nu_s'(CH_3)$ is also modelled.

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