MULTISTAGE VIBRATION - TORSION - ROTATION COUPLING IN THE ν_6 ASYMETRIC N-O STRETCH OF NITROMETHANE

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In the high resolution spectrum of nitromethane near 1584 cm^{-1}each of the zeroth order transitions of the lowest internal rotor state is split into a clump of 4 or 5 rovibrational transitions. Individual perturbing (dark) states are followed as a function of the J', K'_a, and K'_c rotational quantum numbers. Four stages of vibration-torsion-rotation coupling are identified: (i) sub-picosecond c-axis Coriolis coupling to a torsionally excited state dark vibration ($\nu_7 + \nu_{10}$ or ν_5), (ii) a-axis Coriolis coupling between A'_1 and A'_2 torsional states of the dark vibration, (iii) c-axis Coriolis coupling of the dark vibration back to dark rotational states of the asymmetric N-O stretch, and (iv) at J'=8 and higher a strong coupling to a second torsionally excited dark vibration .

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