

NUCLEAR SPIN CONVERSION OF PROPYNE IN SOLID PARAHYDROGEN

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We report observations of propyne (H_3CCCH) nuclear spin conversion (NSC) in solid parahydrogen (para- H_2) at 1.7 K via high-resolution matrix isolation infrared spectroscopy. A rapid vapor deposition technique is used to codeposit room temperature H_3CCCH and precooled para- H_2 gas streams onto a cold substrate maintained below 2.4 K with flow rates that ensure the expeditious growth of monomer-doped solids. This study will focus on the ν_2 and ν_6 modes of propyne in the methyl C–H stretching region near $3.4 \mu\text{m}$, which correspond to parallel and perpendicular rovibrational bands, respectively. For both bands, temporal changes in peak intensities are detected that are characteristic of NSC. In this way, NSC can be used to assign peaks originating from $K=0$ ($A, I=3/2$) and $K=1$ ($E, I=1/2$) levels, even when absorptions are strongly overlapping. Based on these observations, the fine structure observed in these two bands can be assigned to K -rotational structure. At these temperatures, the $K=1$ rotational state should not be populated without nuclear spin restrictions on the total wavefunction. Thus, the slow NSC process allows the $K=1$ level population to be partially trapped in the low-temperature solid. The observation of this NSC process means that the K rotational quantum number is at least partially conserved, indicating H_3CCCH rotates about its symmetry axis in the para- H_2 matrix. The extracted time constant for NSC ($\tau=270(10)$ min) is within an order of magnitude of measurements for other methyl-rotors (H_3CX ; $X = \text{H}$;^a F ;^b OH ;^c $\text{C}(\text{O})\text{CH} = \text{COHCH}_3$ ^d) trapped in para- H_2 matrices, however, this is the fastest rate of relaxation measured to date. These findings are discussed in light of accepted models for NSC and the various rovibrational selection-rules for the above-mentioned molecules.

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