Conformational Switching in Pyruvic Acid Isolated in Ar and N_2 Matrixes: Spectroscopic Analysis, Anharmonic Simulation, and Tunneling

Autorzy

Igor Reva

Cláudio M. Nunes

Małgorzata Biczysko

Rui Fausto

Rok wydania

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Streszczenie

Monomers of pyruvic acid (PA) isolated in cryogenic argon and nitrogen matrixes were characterized by mid- and near-infrared spectroscopy. Interpretation of the experiments was aided by fully anharmonic calculations of the fundamental modes, overtones, and combinations up to two quanta, including their infrared intensities. The initially dominating PA conformer (Tc) has a cis CCOH arrangement and is stabilized by a strong intramolecular H-bond. Selective near-infrared excitation of Tc at the first OH overtone (6630 cm−1 in Ar, 6643 cm−1 in N 2) induced a large scale conformational conversion to the higher-energy conformer (Tt) with trans CCOH arrangement. Tt was then converted back to Tc by selective NIR irradiation at the first Tt OH overtone (6940 cm−1 in Ar, 6894 cm−1 in N 2). In N 2 matrix, the Tt form was stabilized due to interaction between the OH group and the matrix molecules. This stabilization manifested itself in the absence of Tt → Tc relaxation and in a considerable change of the vibrational Tt signature upon going from argon to nitrogen matrix. In argon, the Tt form spontaneously decayed back to Tc in the dark (characteristic lifetime +16 h). In the presence of broad-band near-infrared light, the Tt → Tc relaxation speed considerably increased. The decay mechanisms are discussed.

Słowa kluczowe

Infrared light, Irradiation, Molecular structure, Molecules, Nitrogen

Adres publiczny

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