CFEL SCIENCE

SEMINAR

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CFEL – Building 99, seminar room IV (first floor)

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Rovibrational Transitions of the Methane-Water Dimer from Intermolecular Quantum Dynamical Computations

Rovibrational quantum nuclear motion computations have been carried out [1,2] for the intermolecular degrees of freedom of the methane–water dimer using the GENIUSH code [3] and two intermolecular potential energy surfaces [4,5]. The computations provide the first explanation of the far-infrared spectrum of this complex [6]. The deviation of the experimental and the computed rovibrational transitions (up to J = 2 rotational quantum number) is 0.5 cm^{-1} for the ortho and 2 cm^{-1} for the para species with a variance of 0.005 cm^{-1}. According to the computations, the experimentally reported transitions take place within the 24-fold tunneling splitting manifold corresponding to the zero-point vibration of the global minimum. Most interestingly, theory and experiment agrees about the appearance of negative rotational $J + 1 \leftarrow J$ "excitation" energies. The origin of these negative transition energies, predicted also for the complex of deuterated methane and water, can be rationalized in terms of the monomers' rotational states and the different possible couplings of their angular momenta [2].

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