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Ultrafast vibrational dynamics of BH_4 ions in liquid and crystalline environments

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Borohydrides, currently referred to as “complex hydrides” have been reported for the first time in the 1940s [1,2]. Recently, borohydrides have received increasing attention because of their potential as hydrogen storage materials for mobile applications [3,4]. Processes like phase transitions or hydrogen uptake and release have been investigated intensively but only to a very limited extent the ultrafast dynamics of vibrational excitations [5]. In this talk, the ultrafast vibrational dynamics of the BH_4 ion, the key unit in borohydrides, will be presented [6]. We applied femtosecond infrared spectroscopy in a comparative study of vibrational dynamics in $NaBH_4$ crystallites and in a polar liquid solution containing BH_4 ions. Two-color pump-probe experiments reveal excited state lifetimes of 3 ps for the asymmetric BH_4 stretching mode and of 3.6 ps for the asymmetric bending mode. We provide direct evidence for the BH_4 stretching relaxation pathway via the asymmetric bending mode by probing the latter after excitation of the stretching mode. Pump-probe traces measured in the crystalline phase show signatures of radiative coupling between the densely packed BH_4 oscillators, most clearly manifested in an accelerated subpicosecond depopulation of the excited state of the bending mode. The radiative decay is followed by incoherent vibrational relaxation similar to the liquid phase. The excess energy released in the relaxation processes of the BH_4 intramolecular modes is transferred into the environment with thermal pump-probe signals being much more pronounced in the dense solid than in the diluted solution.

Keywords: *$NaBH_4$; BH_4 ion; ultrafast vibrational dynamics*

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