PROBING THE VIBRATIONAL WAVE PACKET DYNAMICS ON THE ELECTRONIC GROUND STATE OF NEUTRAL SILVER TETRAMER: VIBRATIONAL FREQUENCIES, ANHARMONICITIES AND ANISOTROPY

JIAYE JIN, MAX GRELLMANN, KNUT R. ASMIS, *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie , Universität Leipzig, Leipzig, Germany*.

Small silver clusters possess remarkable luminescence and photoelectric properties, making them subject of current research.[a] However, obtaining vibrations on small, neutral silver clusters remain challenging, due to difficulties in mass-selecting neutral clusters and a lack of easily accessible and widely wavelength-tunable far infrared light sources.

Here, we report our study on experimentally probing the vibrational wave packet dynamics on the ground state potential energy surface of the neutral silver tetramer Ag_4, a benchmark system for small neutral metal clusters, and unambiguously assign its structure. We combine femtosecond pump-probe spectroscopy employing the NeNePo (negative-neutral-positive) excitation scheme[b] with a cryogenic ion-trap tandem mass spectrometer. A linear polarized ultrafast pump pulse ($\sim$40 fs, tunable center wavelength from 700 nm - 820 nm) is used to selectively prepare a coherent wave packet by photodetachment from thermalized (20 - 300 K) Ag_4^- anions. The wave packet dynamics on the electronic ground state are then probed using a second polarized ultrafast pulse ($\sim$50 fs, centered at 400 nm), which ionizes Ag_4 in a two-photon process. The mass-selected cation yield as a function of the delay time (0 - 60 ps) between the two laser pulses yields the fs-NeNePo spectrum. Frequency analysis with a resolution down to about 0.5 cm^{-1} by using Fourier transform of transient traces reveal one prime frequency band (109.5 $\pm$ 0.4 cm^{-1}) in all conditions and four bands at 32 cm^{-1}, 78 cm^{-1}, 186 cm^{-1} and 295 cm^{-1} dependent on pump wavelengths and temperatures. These frequencies are consists with predicted fundamental vibration frequencies (ν_1, ν_2, ν_5 and ν_6) and one combination (ν_1 + ν_2) for rhombic D_{2h} geometry of Ag_4. The rephrasing period of the wave packet allows determining vibrational anharmonicities. A strong dependence of the NeNePo cation signal on the polarization of ultrafast pulses is observed, revealing information on the anisotropy of the partial waves involved in the photodetachment process.

[a] Grandjean, D. et al. Science 2018, 361, 686–690.

[b] Wolf, S. et al., Phys. Rev.Lett. 74(21), 4177; Hess, H. et al., Eur. Phys. J. D, 16(1), 145-149.