Vibrational spectroscopy and dynamics of $W(CO)_6$ in solid methane as a probe of lattice properties

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The phase transition of solid methane is observed through the vibrational spectroscopy of $W(CO)_6$ guest molecule and through its dynamics characterized by time-resolved four-wave mixing experiments. The specificities of the methane lattice are highlighted by surprising behaviors in the vibrational dynamics of the guest in the 5-35 K temperature range.

Solid methane presents a crystalline phase transition at 20.4 K. Although the lattice structure is fcc in both phases, CH_4 molecules are orientationally disordered in phase I (T>20.4K) and partial ordering occurs in phase II (T<20.4K) [1]. Here the T_{1u} CO stretching mode of the $W(CO)_6$ complex isolated in methane is used to study the influence of the solid on the molecular dynamics. A clear temperature behavior is evidenced with linear and non-linear vibrational spectroscopies. The absorption spectrum shows a complex structure explained by the occupancy of different families of trapping sites and exhibits a drastic motional narrowing effect from phase II to phase I. The vibrational dynamics, i.e. population dynamics and dephasing, reveals the coupling of the CO stretching modes with methane, in correlation with the order-disorder properties of the lattice and the lattice motion. The population dynamics in one family of sites is found to be highly dependent on the methane phase, with a shorter lifetime in phase I that can be related to the plastic character of this phase (Fig. 1). Dephasing times of ~130 ps at low temperatures present a smooth shortening upon temperature increase without clear phase dependence. Our results suggest that specific local interactions around the guest monitor the vibrational decoherence and modify the temperature of phase transition. Comparison with our previous works in other cryogenic environments [2] emphasizes the specificities of methane.

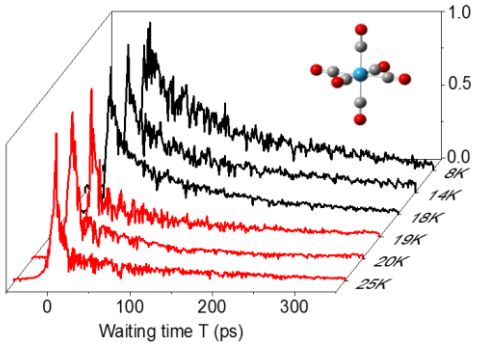

Fig.1 The population dynamics signal of $W(CO)_6$ isolated in solid methane from 8 K to 25 K. Red – recorded in phase I; black – recorded in phase II. A short component appears in phase I that can be related to a family of sites of high symmetry.

[1] W. Press, Single-Particle Rotations in Molecular Crystals; Springer V.; Berlin, Heidelberg, New York, **92** (1981).

[2] R. Thon *et a*l., JPCA **117**, 8145 (2013).