Disentangling matrix site-effects with two-dimensional IR spectroscopy

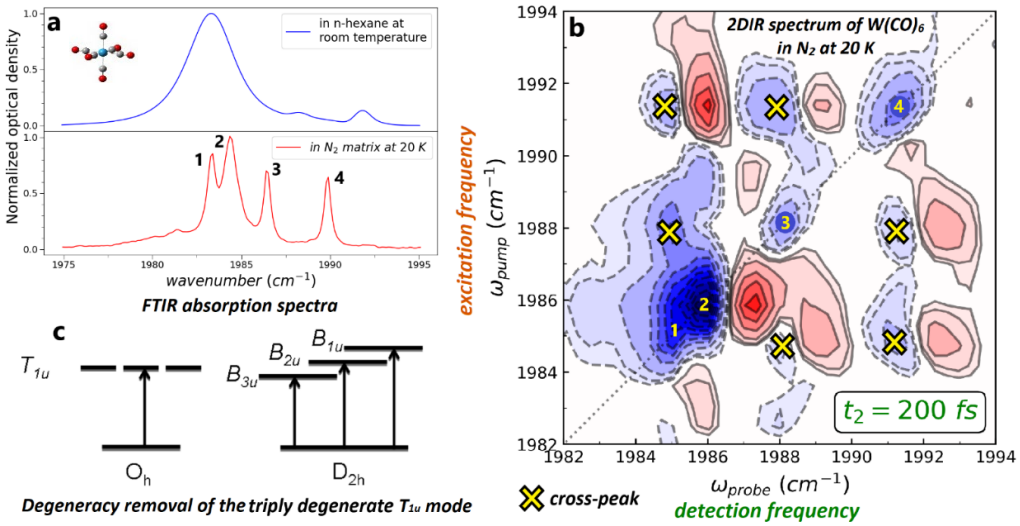
Wutharath Chin[1]*, Armel Jouan[1], Claudine Crépin[1], Jan Helbing [2]

*presenter
[1] wutharath.chin@universite-paris-saclay.fr, ISMO, CNRS, Université Paris-Saclay, France.
[2] Department of Chemistry, University of Zurich, Switzerland.

Two-dimensional infrared (2D-IR) spectroscopy is a powerful tool for investigating structural properties and unraveling molecular vibrational dynamics in different environments. This non-linear technique goes beyond linear absorption spectroscopy by yielding simultaneously structural and dynamical information such as vibrational modes, anharmonicities, vibrational couplings, energy transfers, homogeneous broadening.

We recently obtained the first 2D-IR spectrum in a cryogenic matrix. The IR spectrum of $W(CO)_6$ metal carbonyl complex in nitrogen gives complex structures with thin absorption bands ($\Delta\nu < 1$ cm^{-1}) in the CO stretch region, arising from different families of trapping sites [1]. The high-resolution achieved by 2D-IR setup (< 0.5 cm^{-1}) enables us to unravel this complex band structure in a direct fashion (see figure).

In a 2D-IR spectrum, the FTIR bands can be retrieved from the diagonal peaks, the additional bands provide information on the anharmonicities and electrical or mechanical couplings between vibrations. In the case of $W(CO)_6$ trapped in nitrogen, the cross-peaks (marked as yellow cross) reveal couplings between bands 1, 3, 4, whereas no cross-peak appears with band 2. We interpret this result by the existence of two different families of sites: (i) in the first family linked to band 2, $W(CO)_6$ retains the O_h geometry as in liquid, (ii) in the second family represented by bands 1, 3, 4, the symmetry is broken by the nitrogen lattice, inducing a degeneracy lift of the CO mode. This confirms our prior results in FTIR and photon echo experiments [2]. In addition, the spectra exhibit new interesting features, such as positive anharmonic coupling and coherent excitation transfer between non-degenerate modes.



[1] Graham, M. A., Poliakoff, M.; and Turner, J. J. Photochemistry of the Group VI Hexacarbonyls in Low Temperature Matrices. *J. Chem. Soc. A* **1971**, *0*, 2939.

[2] Thon, R.; Chin, W.; Galaup, J.-P.; Ouvrard, A.; Bourguignon, B.; and Crépin, C. Vibrational perturbations of $W(CO)_6$ trapped in a molecular lattice probed by linear and nonlinear spectroscopy. *J. Phys. Chem. A* **2013**, *117*, 8145.