High-resolution 2D-IR Spectroscopy in Low Temperature Matrix

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Matrix isolation spectroscopy offers an interesting window into vibrational dynamics free from solvent interactions and broad absorption in liquids. The cryogenic temperatures not only allow for new relaxation pathways, but also make it possible to study reactive and less/meta-stable species. Yet the resulting narrow spectral bandwidths (≤1 cm^{-1}) and the matrix site-effects require techniques that can resolve thin, and sometimes complex overlapping features. Our recent high-resolution two-dimensional infrared (2D-IR) spectrometer rises this challenge, opening the route to detailed vibrational signatures and relaxation pathways so far not accessible through classical linear spectroscopy [1].

We report the high spectral resolution 2D-IR spectra of two benchmark metal carbonyls - $W(CO)_6$ and $Fe(CO)_5$ - and bring new insight into the symmetry-breaking these systems undergo in cryogenic matrices.

In solid nitrogen, the T_{1u} (3-fold degenerate) asymmetric C≡O stretch mode of $W(CO)_6$ splits into multiple bands, with 2/3 of molecules showing fully lifted degeneracy (see Fig. 1). 2D-IR cross-peaks reveal weak negative anharmonic coupling (−1 cm^{-1}) and excitation transfer between non-degenerate modes on tens of picoseconds at 20 K, slowing at 5 K. Energy redistribution within high-symmetry T_{1u} modes remains temperature-independent.

The vibrational spectrum of $Fe(CO)_5$ presents an even complex spectrum with dense and overlapping features in cryogenic matrices [2,3]. This richness is unravelled by 2D-IR spectroscopy, revealing multiple trapping sites with different degrees of symmetry breaking. By mapping anharmonicities and mode couplings, we unambiguously assign the numerous transitions into well-defined trapping site families. Going further, we elucidate the ultrafast dynamical processes through polarisation measurements by evidencing site- and mode-specific relaxation, intramolecular energy transfer, and IR activation of dark modes.

Beyond these showcase examples of symmetry-breaking, our high-resolution 2D-IR spectra of matrix-isolated molecules can directly map the anharmonic coupling between normal modes in the fingerprint region, and disentangle complex spectra, making it the method of choice for probing environmental effects in cryogenic matrices.

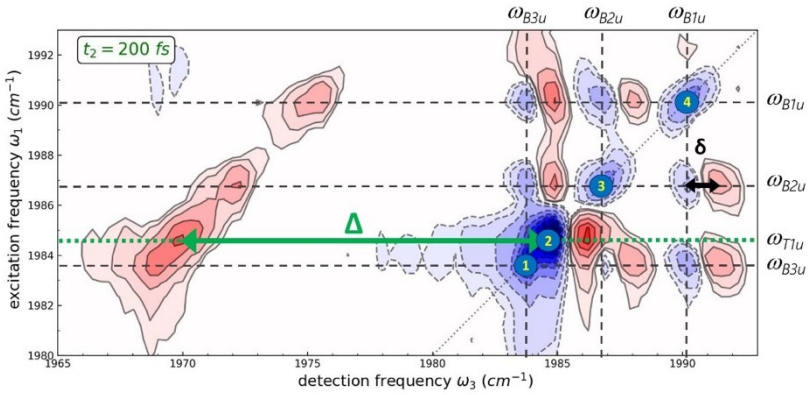

Figure 1: 2D-IR spectrum of $W(CO)_6$ in solid nitrogen at 20 K showing the asymmetric stretch signals for both the degenerate (2) and low-symmetry sites (1,3,4).

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