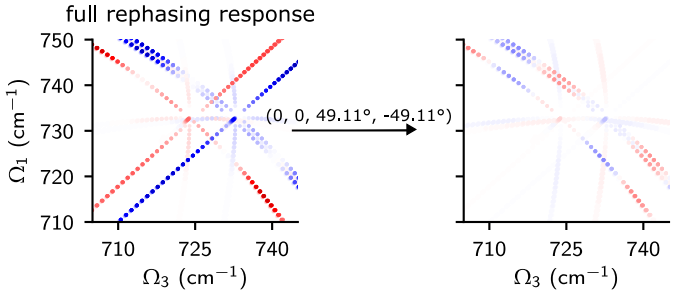
2DIR GAS-PHASE ROVIBRATIONAL SPECTROSCOPY: POLARIZATION DEPENDENCE AND ROTATIONAL COHERENCE EVOLUTION

G. KOWZAN, *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Toruń, Poland*;
T. K. ALLISON, *Departments of Physics and Chemistry, Stony Brook University, Stony Brook, NY 11790-3400, USA*

2DIR spectroscopy is a powerful and well-developed experimental technique, commonly used to study ultrafast molecular dynamics in optically thick liquid-phase and solid-state samples. Newest advances in generation of high-power optical frequency combs in the mid infrared and in cavity enhancement of ultrafast nonlinear signals[1] will enable 2DIR measurements of weakly absorbing samples, in particular of low-concentration gas-phase samples. The high sensitivity of these techniques can be combined with high resolution of multicomb spectroscopy or Fourier-transform spectroscopy to enable measurements of the shapes of individual resonances. In 2DIR liquid-phase spectroscopy of coupled vibrational modes it is common to use sequences of pulse polarizations that eliminate parts of the molecular response and reveal weaker signals. In general, these polarization conditions do not apply to the gas phase. Here, we present polarization conditions that enable control of the gas-phase molecular response[2,3]. We demonstrate their effect on simulations of 2DIR spectrum of the C-Cl stretch in methyl chloride. We also describe the influence of purely rotational coherences evolving during the waiting time and present the ways to exploit them for better separation of signal branches.



[1] doi:10.1039/D1CP00631B, M. C. Silfies *et al*, "Broadband cavity-enhanced ultrafast spectroscopy," Phys. Chem. Chem. Phys. **23**, 9743 (2021).

[2] doi: 10.1103/PhysRevA.106.042819, G. Kowzan and T. K. Allison, "Theory of rotationally resolved two-dimensional infrared spectroscopy including polarization dependence and rotational coherence dynamics," Phys. Rev. A **106**, 042819 (2022).

[3] doi: 10.1021/acs.jpclett.2c03331, G. Kowzan and T. K. Allison, "Controlling Rotationally Resolved Two-Dimensional Infrared Spectra with Polarization," J. Phys. Chem. Lett. **13**, 11650 (2022).

p-number: p219 **Submitted on Fri, 16 Jun 2023 11:19:37 +0200**