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### **Ultrafast two dimensional infrared chemical exchange spectroscopy<sup>1</sup>**

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The method of ultrafast two dimensional infrared (2D IR) vibrational echo spectroscopy is described. Three ultrashort IR pulses tuned to the frequencies of the vibrational transitions of interest are directed into the sample. The interaction of these pulses with the molecular vibrational oscillators produces a polarization that gives rise to a fourth pulse, the vibrational echo. The vibrational echo pulse is combined with another pulse, the local oscillator, for heterodyne detection of the signal. For fixed time between the second and third pulses, the waiting time, the first pulse is scanned. Two Fourier transforms of the data yield a 2D IR spectrum. The waiting time is increased, and another spectrum is obtained. The change in the 2D IR spectra with increased waiting time provides information on the time evolution of the structure of the molecular system under observation. In a 2D IR chemical exchange experiment, two species A and B, are undergoing chemical exchange. A's are turning into B's, and B's are turning into A's, but the overall concentrations of the species are not changing. The kinetics of the chemical exchange on the ground electronic state under thermal equilibrium conditions can be obtained 2D IR spectroscopy. A vibration that has a different frequency for the two species is monitored. At very short time, there will be two peaks on the diagonal of the 2D IR spectrum, one for A and one for B. As the waiting time is increased, chemical exchange causes off-diagonal peaks to grow in. The time dependence of the growth of these off-diagonal peaks gives the chemical exchange rate. The method is applied to organic solute-solvent complex formation, orientational isomerization about a carbon-carbon single bond, migration of a hydrogen bond from one position on a molecule to another, protein structural substate interconversion, and water hydrogen bond switching between ions and water molecules.

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