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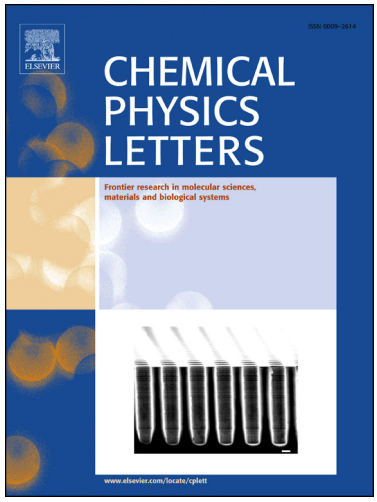

Analytical chemistry, multidimensional spectral signatures, and the future of coherent multidimensional spectroscopy

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Analytical chemistry, multidimensional spectral signatures, and the future of coherent multidimensional spectroscopy

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ABSTRACT

Spectroscopy is a dominant measurement methodology because it resolves molecular level details over a wide concentration range. Its limitations, however, become challenged when applied to complex materials. Coherent multidimensional spectroscopy (CMDS) is the optical analogue of multidimensional NMR and like NMR, its multidimensionality promises to increase the spectral selectivity of vibrational and electronic spectroscopy. This article explores whether this promise can make CMDS a dominant spectroscopic method throughout the sciences. In order for CMDS to become a dominant methodology, it must create multidimensional spectral fingerprints that provide the selectivity required for probing complex samples. Pump-CMDS probe methods separate the pump's measurement of dynamics from a multidimensional and selective probe. Fully coherent CMDS methods are ideal multidimensional probes because they avoid relaxation effects, spectrally isolate the output signals, and provide unique and invariant spectral signatures using any combination of vibrational and electronic quantum states.

1. Introduction

Spectroscopy is an important analytical method for almost every area of science because of its ability to discriminate between the different components in materials over a wide range of concentrations. Vibrational spectra are particularly selective because their numerous, narrow features act as spectral signatures of specific components and moieties. Spectral signatures in this paper are defined either as a single peak or a pattern of peaks that uniquely characterize a single component. Multidimensional NMR methods like heteronuclear multiple quantum coherence (HMQC) have even higher selectivity.[1] These are fully coherent methods that resolve the nuclear spins within specific residues of complex proteins containing thousands of atoms.[2,3] They form the basis for NMR's ability to measure protein structure.[4] The high selectivity results from the formation of multiple quantum coherences (MQCs) between nuclei like ^{1}H, ^{13}C, and ^{15}N. Cross-peaks appear in the multidimensional spectra if the spins are coupled. The chemical shifts of each spin create cross-peaks that act as spectral signatures of specific residues in complex proteins.

A new family of coherent optical spectroscopies were first described in 1997.[5] They were based on the analogue of NMR MQCs. Instead of nuclear spin states, the MQCs in this proposed new family use a mixture of vibrational states to create spectral signatures of materials. MQCs form the basis for the field of Coherent Multidimensional Spectroscopy (CMDS).[6,7] CMDS is proving to be a powerful tool for measuring ultrafast dynamics in a wide variety of systems and it promises to be a transformative technology for revolutionizing the spectroscopic discrimination required for wide-spread dissemination.[8] The future of CMDS depends on two factors that are central to wide-spread dissemination: the ability of CMDS methods to create

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