**John C. Wright**

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July, 2024

Dear Editor,

We enclose a manuscript entitled *Coherent Hyper-Raman Four Wave Mixing Spectroscopies,* authored by Ryan P. McDonnell, Daniel D. Kohler and John C. Wright for consideration as a publication in the *Journal of Chemical Physics* as part of the Y. Ron Shen Festschrift.

The corresponding author is:

Prof. John C. Wright, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, United States of America; email: [wright@chem.wisc.edu](mailto:wright@chem.wisc.edu)

\*CMDS is important and FWM is used to isolate vibrational coupling

\*TWM good for spectroscopy and dynamics – FWM doesn’t have something similar really other than CARS; SIVE comes in and provides upconverted IR spectroscopy

\*SIVE ends up resolving vibronic coupling akin SFG in isotropic systems; unique analogue of hyper-Raman methods

\*Implementation of coherent hyper-Raman == SWM; we have FWM analogue => minimal cascades.

The major innovations of our paper are:

1. Identification of Singly Vibrationally Enhanced (SIVE) spectroscopy as the coherent four wave mixing analogue of hyper-Raman spectroscopy. We show how quantitative analysis of SIVE spectra can resolve the hyper-Raman polarizability *via* the interferometric technique developed by Levenson and Bloembergen.
2. We demonstrate that SIVE spectroscopy is, on average, brighter than its second order analogue, sum frequency generation spectroscopy, making it a feasible method for interpreting isotropic spectra of most vibrational species.
3. We demonstrate the feasibility and properties of SIVE spectroscopy by probing vibrations in a thin film of cyanocobalamin (i.e. Vitamin B12). It is found that the hyper-Raman polarizability significantly modulates the relative intensity of the SIVE output in non-resonant and resonant cases.

We believe this manuscript highlights the versatility of mixed time-frequency domain methods as a probe of molecular structure and will be of great interest to the readership of *The Journal of Chemical Physics*. This work has a direct impact on the development of multidimensional spectroscopies and provides new methods for investigating vibronic coupling in molecular species. We believe this work will encourage the implementation of mixed time-frequency domain methods for probing noncovalent interactions and ultrafast dynamics in material and biomolecular systems, chemical reactions, and probing vibronic coupling in complex molecular systems.

Sincerely,

A close-up of a black handwritten letter

Description automatically generated

John C. Wright

Andreas C. Albrecht Professor of Chemistry

University of Wisconsin - Madison

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P.S. We suggest the following reviewers:

**Prof. David A. Blank**

Department of Chemistry

University of Minnesota

Email: [blank@umn.edu](mailto:blank@umn.edu)

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Reason: Prof. Blank is an expert in the application of mixed vibrational/electronic spectroscopies.

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**Prof. Minhaeng Cho**

Center for Molecular Spectroscopy and Dynamics

Institute for Basic Science, Korea University

Email: [mcho@korea.ac.kr](mailto:mcho@korea.ac.kr)

Website: [cmsd.ibs.re.kr/html/cmsd\_en/](https://cmsd.ibs.re.kr/html/cmsd_en/)

Reason: Prof. Cho is an expert in the theory of the coherent multidimensional spectroscopies discussed in this manuscript.

**Dr. Paul M. Donaldson**

Senior Scientist

UKRI Central Laser Facility

Email: [paul.donaldson@stfc.ac.uk](mailto:paul.donaldson@stfc.ac.uk)

Website: [www.clf.stfc.ac.uk/Pages/paul\_donaldson\_ukri\_fellow.aspx](http://www.clf.stfc.ac.uk/Pages/paul_donaldson_ukri_fellow.aspx)

Reason: Dr. Donaldson is a pioneer and expert in the application of coherent Raman spectroscopies to biomolecular samples.

**Dr. Maksim Grechko**

Group Leader, Max Planck Institute for Polymer Research

Email: [grechko@mpip-mainz.mpg.de](mailto:grechko@mpip-mainz.mpg.de)

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Reason: Dr. Grechko is an expert in the design and application of the coherent multidimensional spectroscopies discussed in this manuscript.

**Prof. Anne Myers Kelley**

School of Natural Sciences

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Email: [amkelley@ucmerced.edu](mailto:amkelley@ucmerced.edu)

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Reason: Prof. Myers Kelley is a pioneer and expert in the application and theory of resonance Raman and hyper-Raman spectroscopy to condensed phases.

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**Prof. Roseanne Sension**

Department of Chemistry and Department of Physics

University of Michigan

Email: [rsension@umich.edu](mailto:rsension@umich.edu)

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Reason: Prof. Sension is an expert in transient infrared and visible spectroscopy, and the spectroscopy of cyanocobalamin.

**Prof. Patrick Vaccaro**

Department of Chemistry

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Email: [Patrick.Vaccaro@yale.edu](mailto:Patrick.Vaccaro@yale.edu)

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Reason: Prof. Vaccaro is an expert in the application and theory of non-degenerate, coherent four wave mixing spectroscopies.

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**Prof. Lawrence D. Ziegler**

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Reason: Prof. Ziegler pioneered resonance hyper-Raman spectroscopy.