**John C. Wright**

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Dear Editor,

We enclose a manuscript entitled *Coherent IR-Hyper-Raman Four Wave Mixing Vibrational Spectroscopy,* 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.

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Four wave mixing (FWM) spectroscopies are largely known for their ability to dissect vibrational anharmonicity in large and small molecular species. For example, these methods can resolve anharmonic coupling though infrared (2D-IR) and infrared/Raman (Doubly Vibrationally Enhanced) pathways. These methods were based upon coherent anti-Stokes Raman spectroscopies (CARS) developed in the 1970 and 1980’s. Similarly, three wave mixing (TWM) methods resolve interfacial vibrational spectroscopy and dynamics through infrared/Raman pathways (sum frequency generation). A seldom used type of transition which could increase the specificity of nonlinear spectroscopy are hyper-Raman transitions. However, unlike CARS, the coherent analogue of pure hyper-Raman spectroscopy is a six wave mixing technique, which is virtually impossible to resolve in the laboratory due to lower order, four wave mixing cascades that complicate output. The only example of an infrared/hyper-Raman type method was developed in our laboratory decades ago to demonstrate the feasibility of four wave mixing involving solely vibrational transitions, but has not been investigated in detail for over twenty years.

Very recent experiment work from our laboratory and Mischa Bonn’s laboratory has made it clear that hyper-Raman based FWM spectroscopies are present in and interfere with infrared/Raman FWM spectroscopies. However, the parameters which drive this infrared-hyper-Raman hybrid spectroscopy have not been explored. To this end, we have investigated the parameters which drive nonlinear output in the infrared/hyper-Raman type spectroscopies and identified gross selection rules. The spectroscopy has been called hyper difference frequency generation (HDFG), due to its similarity to difference frequency generation. We have shown that the HDFG methods allow output for any harmonically allowed, infrared active vibration. Since the methodology is only dependent upon single quantum coherences, this makes HDFG a potential probe of single quantum coherence lifetimes in isotropic media without need for anharmonicity. We have identified methods for using FWM to quantify the hyper-Raman hyperpolarizability, negating the need for complex spontaneous hyper-Raman experiments to probe vibrational hyperpolarizabilities.

The major innovations of our paper are:

1. Identification of hyper difference frequency generation (HDFG) spectroscopy as the coherent four wave mixing analogue of hyper-Raman spectroscopy. This bypasses the need for six wave mixing techniques to access hyper-Raman properties of infrared active vibrations. HDFG is found to be allowed for all harmonically allowed infrared vibrations.
2. Through the use of the hyper-Raman *A,B,C* coefficient expansion developed by Chung and Ziegler (*J. Chem. Phys.* **88**, 7287-7294 (1988)), the selection rules of HDFG are identified and discussed. It is found that HDFG is an example of a site-selective spectroscopy for infrared active vibrations. The vibronic structure of electronic states and their couplings to specific vibrational modes could be assessed through this technique.
3. The feasibility of HDFG as a four wave mixing technique for practioncers of vibrational sum frequency generation (vSFG) spectroscopy. We show, through a simple calculation, that vSFG and HDFG have roughly an equivalent output polarization in a transmission geometry. Laboratories which perform vSFG studies should also be able to perform HDFG, using roughly an identical setup, to resolve spectra and dynamics in the bulk.
4. By using the interferometric technique developed by Levenson and Bloembergen (*J. Chem. Phys.* **60,** 1323-1327 (1974)) and a simple treatment of orientational averaging, it is shown that HDFG can extract hyper-Raman polarizabilities of infrared active vibrations. This should ease the experimental determination of hyper-Raman hyperpolarizabilties and provide a comparison point for theoretically predicted vibrational hyperpolarizabilities.

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

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Andreas C. Albrecht Professor of Chemistry

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P.S. We suggest the following reviewers:

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

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Reason: Prof. Cho is an expert in the theory of CMDS.

**Dr. Paul M. Donaldson**

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

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

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Reason: Prof. Myers Kelley is a pioneer and expert in condensed phase resonance hyper-Raman spectroscopy and four-wave mixing spectroscopy.

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