**John C. Wright**

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September 24, 2024

Dear Professor Ogilvie,

We enclose our edits and responses to reviewer comments regarding our 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.

The corresponding author is:

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We appreciate the thorough peer review of our work. We believe that our revised manuscript addresses the reviewer concerns and meets the high standards and broad impact of *The Journal of Chemical Physics*. Please see the end of the document for our responses to the reviewer comments.

This manuscript highlights the feasibility and applicability of hyper-Raman based four wave mixing spectroscopies to solving modern problems related to electronic-vibrational coupling, and we believe, as noted by both reviewers, 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. 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. Therefore, in agreement with both reviewers, we believe our updated manuscript is suitable for publication in T*he* *Journal of Chemical Physics.*

We hope that our responses to the reviewer comments meet your high standards, and we look forward to publication in the *The* *Journal of Chemical Physics.*

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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We thank the reviewers for their assessment of our work. They have prompted us to understand subtle aspects of the HDFG process more deeply, which has yielded a more insightful description of the HDFG output. While the responses to the reviewer comments can be found below, here we list some major changes to the manuscript that we have made during the revision process which do not exactly correspond to specific reviewer comments.

* We have added a section on calculating static inhomogeneity in HDFG response to the manuscript, following the methods developed individually by Hudson, Hochstrasser, and Wright (lines 250-279)
* We now plot the Real and Imaginary parts of the HDFG response (Figures 3c, d) to provide further insight into how constructive and destructive interference manipulates the overall HDFG spectrum.
* A Supporting Information (SI) document has been added. In the SI, we: generate an expression for calculating Herzberg-Teller integrals using Hermite polynomial recursion formulae, discuss the impact of Franck-Condon and Herzberg-Teller integral on the HDFG spectra, investigate the impact of potential well offset and other molecular parameters on HDFG spectra, and provide detailed evaluation of the integrals which dictate static inhomogeneity for HDFG.
* We found that the Herzberg-Teller integrals used in the first draft of the manuscript were incorrect (which motivated the discussion of Herzberg-Teller integral calculation in the supporting information). We have carefully checked all the Franck-Condon and Herzberg-Teller integrals used in the text.
* Discussion on the sign of the molecular parameters used in the HDFG spectrum simulation, as well as the impact of orientational averaging on the overall signal, has been added to the main text and SI.

Reviewer Comments:

Reviewer #1 Evaluations:   
Recommendation: Major revision   
New Potential Energy Surface: No   
Overall Rating (required): Top 25-50% - significant and/or novel contribution of broad interest with potential for impact   
  
Reviewer #1 (Comments to the Author):

Re: JCP24-AR-SHEN2024-03423, McDonnell, Kohler, and Wright, “Coherent IR Hyper-Raman Four Wave Mixing Spectroscopy”

This theoretical paper discusses hyper difference frequency generation (HDFG), a variation on four- wave mixing spectroscopy that involves both infrared absorption and hyper-Raman resonances. HDFG uses a similar experimental configuration to sum frequency generation but does not require a noncentrosymmetric medium. This manuscript clarifies the selection rules and the sources of intensity for HDFG and presents a model calculation of the frequency dependence of the signal. The manuscript is well motivated and generally well written, but I find it rather lacking in depth and completeness as a paper with no experimental data.

Author Response:

We thank the reviewer for their interest in our manuscript and their detailed comments.

Below are some specific comments:

1. The lengths and colors of the arrows in Fig. 2 are confusing. Presumably these are supposed to indicate different time orderings of the interactions of the same three applied fields with the sample. In five of the six parts, the orange arrow (2) is shorter (lower frequency) than the red arrow (3), but in 2(a) the lengths of the two arrows are transposed. Shouldn’t the 2 and 3 arrow lengths in (a) be switched and the energy of the virtual state |m,n> be lowered?

Author Response:

Thanks for catching this. The WMEL diagrams in Figure 2 in the old version of the draft used virtual states which ‘floated’ in energy. We have addressed this problem by making a new figure where the virtual state placements are dependent upon the input beam color.

1. Eq. (3) for the HDFG hyperpolarizability assumes that all coherences decay with a purely exponential time dependence. This would result in both vibrational and vibronic transitions having a Lorentzian lineshape. This is sometimes a pretty good approximation for vibrational transitions, but almost never for vibronic transitions of medium sized to large molecules or nanoparticles in ambient temperature solutions, which I assume would be the most likely targets for these techniques. In most such systems the dephasing, dominated by solvent-solute interactions rather than lifetime decay, has a non-exponential time profile leading to non-Lorentzian lineshapes. The incorporation of realistic dephasing functions into four-wave mixing calculations has been discussed in detail by Mukamel in the 1980s and 1990s, as well as others. Nonexponential vibronic dephasing should be considered here, or else the authors should clearly state the class of physical systems for which purely Lorentzian vibronic broadening is a good approximation.

Author Response:

We thank the reviewer for these points about lineshapes. Indeed, the groups of Shaul Mukamel, Anne Myers Kelley, among others, have developed detailed methods to understand inhomogeneous broadening in coherent and incoherent Raman experiments (e.g., 10.1021/j100328a010, 10.1021/ja00103a020). We have added some discussion in the introduction of our manuscript to make it clear that this manuscript is working in the exponential dephasing limit by assuming sufficiently long laser pulses. This limit has been found to be appropriate for experimental work investigating doubly resonant sum frequency generation by Shen and coworkers (doi: 10.1016/S0009-2614(02)00560-2), as well as theoretical work investigating 2D-EV and 2D-VE spectroscopy by Gaynor and Khalil (doi: 10.1063/1.4991745). We have added significant discussion regarding these ideas to the manuscript in lines 83-94.

1. Similarly, the authors do not address the effect of vibronic inhomogeneous broadening on the spectra, yet inhomogeneous broadening typically makes a considerable contribution to the overall vibronic width for most glassy or solution phase systems and will certainly affect plots such as Fig. 3(b). This needs to be addressed. I found only one mention of inhomogeneous broadening in the manuscript, near the bottom of page 3, and no follow-up.

Author Response:

The reviewer is correct; this is an oversight of the previously submitted manuscript. We have added a section on inhomogeneous broadening in the manuscript to investigate how HDFG lineshapes inform on the correlations between vibronic and vibrational features. For correlated vibrations and vibronic in particular, due to the presence of a rephasing pathway, HDFG linenarrows inhomogeneously broadened transitions akin to difference frequency generation, as first discussed by Dick and Hochstrasser (doi: 10.1063/1.445086). For anti-correlated modes, there is no line-narrowing, and the inhomogeneous lineshape dominates the response. We have added a section to the manuscript to discuss these effects (see newly added lines 262 – 290) and provide explicit derivations of line broadening mechanisms to the supporting information.

1. Simulated spectra in Fig. 3(b) are shown for one set of parameters. The authors should explain why they chose those parameters—specifically, the vibrational frequency of 2200 cm-1 (an unusual frequency for a vibrational fundamental), the dimensionless displacement of  = 0.5, and the vibronic homogeneous linewidth of 700 cm-1. I also note that a Lorentzian vibronic lineshape with a 700 cm-1 width is very nearly unheard-of; see #2 above. It would also be helpful to show a few plots, perhaps in the SI, for other values of these parameters.

Author Response:

Thanks for these comments. The values in the main text were initially chosen arbitrarily to illustrate the HDFG spectrum. We have since recreated the figure in the main text to use 1600 cm-1 (i.e. carbonyl frequency) and 400 cm-1, while keeping = 0.5. In the newly created supporting information, we used values from Myers et al. and Brennan et al. to simulate expected HDFG spectra based upon different } values.

The development of the A, B, and C terms in Section II.B. is clear and consistent with previous work on spontaneous Raman and hyper-Raman scattering. I appreciated the discussion of the dependence of the A and B terms on vibronic detuning immediately above Table I.

Author Response:

We appreciate these comments, and hope that other readers find the discussion of pre-resonance effects useful as well.

In conclusion, this manuscript presents a basic theoretical description of a variation on resonant four- wave mixing that could prove to be useful but has not yet been explored much. I think that this manuscript could be made suitable for JCP if the treatment of vibronic broadening were fleshed out to be applicable to the types of physical systems that would most usefully be studied with this method.

Reviewer #2 Evaluations:   
Recommendation: Optional revision   
New Potential Energy Surface: No   
Overall Rating (required): Top 25-50% - significant and/or novel contribution of broad interest with potential for impact   
  
Reviewer #2 (Comments to the Author):   
  
The manuscript by McDonnell et al. discusses selection rules and possible application of hyper difference frequency generation spectroscopy. This method can help elucidating coupling between molecular electronic and vibrational degrees of freedom, which is central for electron dynamics in molecular systems. The manuscript is clear and can help researches in the field of chemical physics in designing new spectroscopy experiments. I think that this work is suitable for The Journal of Chemical Physics. I have few minor remarks that the authors can address.

Author Response:

We thank the reviewer for their interest in our proposed method and their helpful comments below.

1) When discussing different spectroscopy techniques that allow measuring vibrational and electronic coupling (first paragraph of the Introduction section), the authors do not mention two-dimensional electronic-vibrational (2D EV) and vibrational-electronic (2D VE) spectroscopies developed in the groups of Graham Fleming and Munira Khalil, respectively. I believe that these methods are part of the state-of-the-art relevant to the presented discussion and the original works should be referenced.

Author Response:

We apologize for overlooking these works; indeed, they are incredibly relevant to this manuscript and deserve discussion in the introduction. We have cited the original works by the Fleming and Khalil groups, as well as the 2D-EVSFG technique developed by Rao and colleagues and added some new discussion to the introduction.

Text added on Page 2:

Nonlinear spectroscopic probes of electronic-vibrational coupling are not limited to the Raman and hyper-Raman based techniques diagrammed in Figure 1. Independently developed by the Fleming and Khalil groups, respectively, 2D Electronic-Vibrational (2D-EV) and 2D Vibrational-Electronic (2D-VE) spectroscopy are based upon pump-probe and absorption type pathways which also investigate e-v coupling. The Rao group has also developed a *χ*(4) analogue of 2D-EV, 2D-EV sum frequency generation (2D-EVSFG), to investigate interfacial e-v coupling. These methods have been used to investigate vibronic coupling in a variety of molecular systems and serve as 2D pump-probe type analogues to the hyper-Raman-based spectroscopies discussed here.

2) On page 7, there is an explanation why the inner product of wavefunctions is zero: "This follows from ... , for wells with identical curvature". Actually, this has more general origin. When the two wells are identical, they have the same vibrational Hamiltonian. Hamiltonian is a Hermitian operator, and eigenstates of a Hermitian operator with different eigenvalues are orthogonal (their inner product is 0).

Author Response:

We thank the reviewer for making this point. These ideas have been moved to the supporting information, where we expand much more on the impact of different values.  
  
3) On the same page 7: "In the pre-resonant region, both A and B terms die off...". Why in this sentence the first index of "delta" is (e0), and not (ev')?

Author Response:

The reviewer is absolutely correct; this was an unfortunate mistype on our end. Additionally, to make the text cleaner, we added tildes to all states on an excited surface, making the proper term .