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. 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?
2. 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.
3. 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.
4. 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.

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.

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.   
  
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 should be discussed in some detail in the introduction. We have cited the original works by the Fleming and Khalil groups () and added some new discussion to the introduction.

Text added: words

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:

Thank you for making this point. The text has been modified so this is made obvious to the reader.

Old Text: Words

New Text: words  
  
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:

This was an unfortunate mistype on our end. The proper term should be . Thank you for catching it. We have carefully checked the manuscript to ensure any similar mistypes have been addressed. These are found in the marked-up manuscript, but we list them here for clarity.

List of corrected statements: