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Authors

Harbola, Upendra
Agarwalla, Bijay Kumar
Mukamel, Shaul

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Response to “Comment on ‘Frequency-domain stimulated and spontaneous light emission signals at molecular junctions’” [J. Chem. Phys. 142, 137101 (2015)]

Upendra Harbola,¹ Bijay Kumar Agarwalla,² and Shaul Mukamel²

¹Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

²Department of Chemistry, University of California, Irvine, California 92697, USA

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Two types of issues were raised by Galperin, Nitzan, and Ratner (GRN). (1) The correct formal diagrammatic definition of the stimulated light emission (SLE) signal in terms of molecular correlation functions and the identification of the sub-set of diagrams that contribute to the Raman signal. (2) What approximations are used to actually compute these correlation functions in the presence of electron currents in a junction, including broadening and the renormalization of molecular correlation functions due to lead interactions. Note that the signal is computed perturbatively in the interaction with the radiation field, and therefore, there is no renormalization with respect to the molecule-field interaction. Regarding point (2) we note that in Ref. 1, we have adopted a quantum master equation (QME) approach due to its simplicity. This is not a limitation of the superoperator formulation. Indeed, a nonequilibrium Green's function approach is also available in Liouville space^{2,3} which can account for the effects of broadening due to the lead-molecule interaction. Different approximations may hold in different parameter regimes but this depends on details of the model and will not be addressed here. Below we focus solely on more fundamental issue (1) for which there is a clear cut unambiguous answer.

The superoperator loop diagram approach of Ref. 1 is the correct and the more transparent formulation of spontaneous optical signals from molecular junctions. It provides a systematic bookkeeping of time ordering. Our final diagrams do differ from those considered in Ref. 4. The Liouville space superoperator technique for computing optical signals from molecules is well established. We have shown³ that the Hilbert space Green's function Keldysh contour technique is formally identical to the Liouville space loop diagrams. However, the latter approach is more intuitive and physically transparent. As stated in Ref. 1, Ref. 4 includes a diagram (Fig. 8(b)) which does not contribute to SLE and misses other diagrams that do contribute. It is not clear how these diagrams were selected. In our approach, we systematically include the right diagrams and discuss the underlying physics, leaving no room for ambiguities. Below is our response to the specific points raised by GRN.⁵

Equation (1) in Ref. 5 is the same (in Hilbert space) as Eq. (A1) in Ref. 1 (in Liouville space). However, one must be careful as the Hilbert space formulation (Eq. (1) in the GRN comment) includes a mixture of the loop and physical times.

A real time close-time-path loop (CTPL) formulation exists which can avoid artificial loop time of Keldysh approach.⁶ However, the CTPL technique is also based on the forward and the backward time evolutions in Hilbert space. This has been discussed in our earlier work.³ On the other hand, the Liouville space formulation avoids both the artificial time as well as the backward evolution in real time, making it easier to interpret diagrams and, in this particular case, to identify contributions to Raman and fluorescence. Our main criticism of Ref. 4 is related to the incorrect identification of diagrams that contribute to the Raman signal in molecular junctions. We have no issue with the Keldysh method which can be exactly mapped into the Liouville space formulation (see Ref. 3 and references therein). However, we wish to emphasize that Liouville space approach presents a more transparent formulation that is less prone to misinterpretations. We believe that this has been the case in Ref. 4 where certain diagrams have been erroneously assigned to fluorescence and therefore discarded in calculating the Raman signal.

In Ref. 5, GRN mention that we consider the diagrams shown in Fig. 1. These diagrams are not discussed in Ref. 4. Indeed, both approaches, if formulated correctly, must give the same number of diagrams as the underlying physics is identical. According to their mapping between our diagrams and theirs, only diagrams in Figs. 1(b) and 1(d) in Ref. 1 should contribute to the Raman. We show in Ref. 1 that all diagrams in Fig. 1 of Ref. 1 contribute to the Raman process.

As stated in Ref. 5, only in-scattering diagrams for the incoming mode i ($F_i^<$) are considered which, according to them, correspond to Figs. 1(a), 1(b), and 1(d) in Ref. 1. However, no explanation is given as to why Fig. 1(c) should not contribute, except that it gives Raman scattering without the incoming field. This is an incorrect interpretation of our diagrams. All diagrams in Fig. 1 of Ref. 1 contribute only in the presence of the incoming field (see Eqs. ((9)-(12)) in Ref. 1). The incoming field interacts in four possible ways, generating 4 loop diagrams (two interactions from the ket side, two from the bra side, and one each from ket and bra). We identify Raman resonances by the argument in the Green's function of the type $\omega_1 \pm \omega_2 = \omega_{ab}$ where ω_1 and ω_2 are the frequencies for incoming and spontaneously detected modes, respectively. All diagrams in Fig. 1 in Ref. 1 contain such resonances. As mentioned in Ref. 5, the excited electronic states can

be populated by the interaction with the lead; however, this excited state can decay via a fluorescence pathway and this can happen without the incoming external field. Indeed, in the presence of an external field, there is a competition between the Raman and fluorescence pathways. The SLE signal from an isolated molecule is generated by a stimulated absorption at ω_1 and a subsequent emission at ω_2 which can happen both coherently (Raman) and incoherently (fluorescence). Similarly, in a molecular junction where initially the molecule can be in an excited state, in addition to above processes, a stimulated emission at ω_1 and a subsequent emission at ω_2 can occur either coherently or incoherently. Therefore, diagrams in Figs. 1(a) and 1(c) of Ref. 1 also contribute to Raman as well as to fluorescence signal. Our formulation clearly shows how to distinguish these various contributions. This is an important difference between equilibrium and non-equilibrium (molecular junction) spectroscopies which GRN seem to have missed. According to their mapping of diagrams shown in Fig. 1(b), it is clear that they have missed the Raman contributions from processes represented in diagrams (a2), (a3), (a5), (a6), (b5), (b6), (c2), (c3), (c5), (c6), and one of the contributions in A2.

The superoperator loop diagram approach of Ref. 1 offers a more transparent formulation of spontaneous optical signals from molecular junctions.

In summary, in Ref. 1, we have presented a Liouville space diagrammatic formulation to compute spontaneous and stimulated signals from a molecular junction. We disagree with the claim made in Ref. 5 that we do not distinguish between the Raman and fluorescence contributions. The superoperator approach uses a different bookkeeping protocol than the Keldysh formalism. The nature and role of the various time variables is more transparent, suggesting different physically motivated approximations that are directly linked to the wavefunction or to the density matrix of the system.

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