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Permalink
https://escholarship.org/uc/item/9607g5mp

Journal
The Journal of Chemical Physics, 142(13)

ISSN
0021-9606

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Publication Date
2015-04-07

DOI
10.1063/1.4916523

Peer reviewed

Comment on "Frequency-domain stimulated and spontaneous light emission signals at molecular junctions" [J. Chem. Phys. 141, 074107 (2014)]

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(Dated: 12 December 2014)

We discuss the derivation of the optical response in molecular junctions presented in U. Harbola et al., J. Chem. Phys. **141**, 074107 (2014) which questions some terms in the theory of Raman scattering in molecular junctions developed in our earlier publications. We show that the terms considered in our theory represent the correct contribution to calculated Raman scattering and are in fact identical to those considered by Harbola et al. We also indicate drawbacks of the presented approach in treating the quantum transport part of the problem.

In their recent publication Harbola et al.[1] criticize our earlier treatment of Raman spectroscopy in molecular junctions,[2–5] claiming that: 1. Diagrams (a) and (c) in Fig. 8 of our Ref. 3 are incomplete contributions, while (b) does not contribute to the Raman signal and 2. Diagrams with the two incoming field modes on the same branch are missing. Below we show that the criticism is based on a misunderstanding.

Raman signal in molecular junctions is a coherent process of 4th order in coupling to the radiation field (couplings are to the outgoing, f, and and incoming, i, photons)

$$J_f(t) \equiv \frac{d}{dt}\langle \hat{a}_f^\dagger(t)\hat{a}_f(t)\rangle = |U_f|^2 \, 2\text{Re}\int_{-\infty}^t dt' \, e^{i\nu_f(t-t')}\langle \hat{O}^\dagger(t')\,\hat{O}(t)\rangle \tag{1}$$

$$= |U_i|^2 |U_f|^2 \, 2\,\text{Im} \int_{-\infty}^t dt' \int_c d\tau_1 \int_c d\tau_2 e^{i\nu_f(t-t')} \, F_i(\tau_1,\tau_2)\,\langle T_c\,\hat{O}^\dagger(t')\,\hat{O}(t)\,\hat{O}^\dagger(\tau_1)\,\hat{O}(\tau_2)\rangle$$

Here $\hat{a}_f^\dagger$ $(\hat{a}_f)$ are creation (annihilation) of photon in the mode f, ν_f (ν_i) is frequency and U_f (U_i) is molecular coupling to the outgoing (incoming) mode. $\hat{O}$ is the molecular de-excitation operator, $\tau_{1,2}$ are the Keldysh contour variables, T_c is the contour ordering operator, and $F_i(\tau_1,\tau_2) \equiv -i\langle T_c\hat{a}_i(\tau_1)\hat{a}_i^\dagger(\tau_2)\rangle$ is the free photon function of the mode i. Second line in Eq. 1 results from 2nd order perturbation theory in coupling to the mode i.

Eq. (1) (this is Eq.(26) in Ref. 3) is identical to the expression derived in Ref. 1. The fact that the two papers yield the same expression is not surprising, since both Keldysh technique (used in our paper) and Liouville space formulation (used by Harbola et al.) are known to be equivalent.[6–9] Different diagrams are obtained by considering all possible placements of the contour variables τ_1 and τ_2 between fixed (on the contour) real times t and t'. There are 24 such diagrams (12 are shown in Fig. 1, the other 12 are their complex conjugate versions). The correspondence between the diagrams in Fig. 1 and those in Fig. 1 of Ref. 1 is the following: A1 and B1 correspond to diagram (a), A4, A5, A6, B4, B5, B6 yield (b), B2 and B3 correspond to (c), and A2 and A3 yield (d).

We stress that the flux in Eq. (1) is *the total optical signal.* Contributions can be separated into fluorescence, renormalization of molecular correlation functions (virtual photon processes), and Raman. Harbola et al. utilize all these diagrams (including reducible, i.e those of repeated second order processes) in their consideration, and from their reply to this comment it appears that they do not make this distinction. We focused on the Raman signal only, disregarding fluorescence and renormalization diagrams. For the Raman process one has to keep only in-scattering diagrams for the mode i ($\sim F_i^<$). These are diagrams A
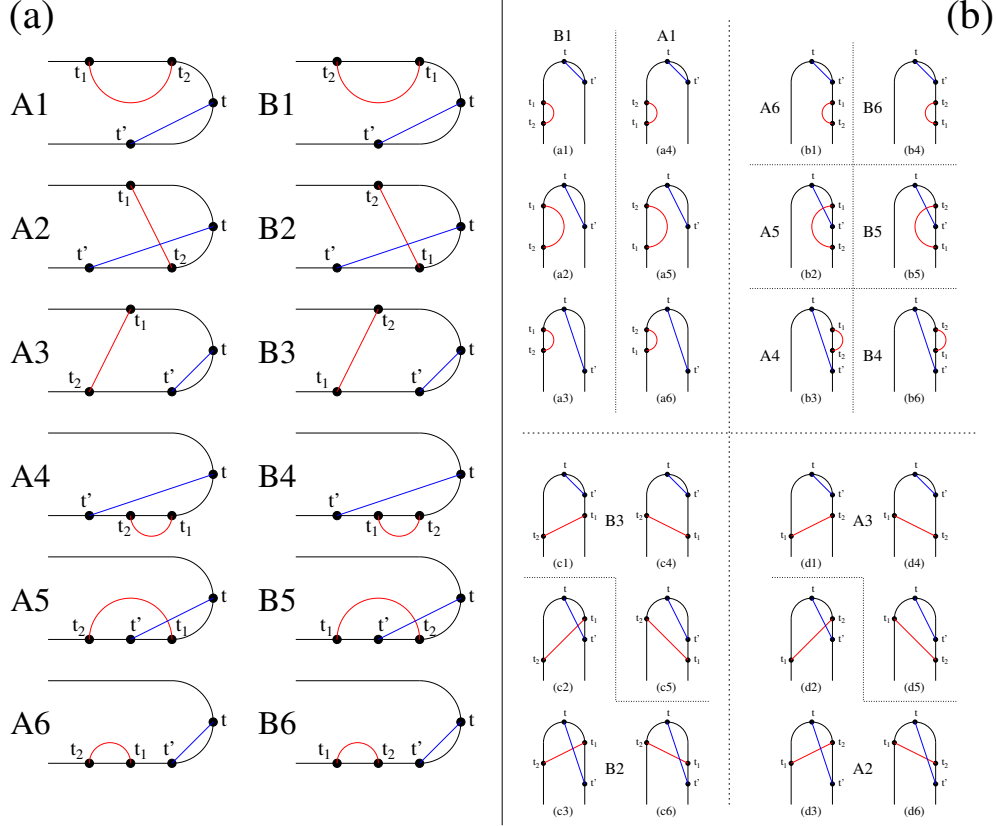
FIG. 1. (a) Diagrams for the fourth order interaction with the modes i (red) and f (blue) of the optical field and (b) their comparison to the diagrams presented in Figs. 1, 4 and 5 of Ref. 1.

in Fig. 1. Note that in contrast to what may be inferred from the reply to this comment[10] considering diagrams $\sim F_i^>$ would mean existence of Raman scattering even in the absence of the pumping field (by pumping field we mean processes of excitation in the molecule due to absorption of the incoming photon). Clearly, optical process in a junction in the absence of the pumping field is possible due to population of the excited states by the applied bias (e.g. bias induces fluorescence). However, such processes do not represent Raman scattering.

In Refs. 2 and 3 we considered a two-level model with linear coupling to molecular vibration. Within this model, the correlation function can be splitted approximately into product of pure electronic correlation function and the generalized Franck-Condon factor (see Eqs. (26)-(30) of Ref. 3). At steady state the first integral in Eq. (1) leads to delta functions that represent energy conservation. We kept only those contributions to the total signal whose energy conservation has the form $\delta(\nu_i - \nu_f + n\omega_v + \Delta E)$. Here n is integer number, ΔE is electronic energy change within the same broadened level, and ω_v coming

from the generalized Franck-Condon factor.

There are only 4 processes satisfying both in-scattering of the incident mode and the required energy conservation conditions, and together they correspond to the total Raman signal. These are processes coming from diagrams A2, A3, A4, and A5 diagrams of Fig. 1, which corresponds to (c), (a), (b), and (c) diagrams of Fig. 8 of Ref. 3, respectively. To see this one has to employ Langreth rules.[11] The rules yield 4 terms for diagram A4

$$\int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t) \int_{-\infty}^{0} d(t_2-t_1)\ldots - \int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t) \int_{-\infty}^{0} d(t_2-t')\ldots -$$
$$\int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t') \int_{-\infty}^{0} d(t_2-t_1)\ldots + \int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t') \int_{-\infty}^{0} d(t_2-t')\ldots$$

$$(2)$$

and only 2nd of these integrals gives contribution to Raman by the above criteria. Similarly, A3 is given by one, while A2 and A5 by two integrals. Evaluating relevant integrals one gets the normal and inverse Raman signals, and their interference (see Fig. 8 of Ref. 3).

We now comment on positions of times (t, t', t_1, t_2) in the diagrams. It is true, that in general (when explicit time-dependent processes or a magnetic field are present), the time t of the signal should be the last time of a diagram (see Fig. 1). Diagram (b) in Fig. 8 of Ref. 3 (analog of A4 in Fig. 1) is different. Its form represents 'the hole view' of scattering process. One can show that in the steady state situation considered in our papers the two diagrams are equivalent. Indeed, the contribution of diagram A4 to the Raman signal is (note, it is easy to see that the contribution is real following the derivation leading form Eq.(28) to Eq.(56) in Ref. 3) $|U_i U_f|^2 N_i \int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t) \int_{-\infty}^{0} d(t_2-t') e^{i\nu_f(t-t')-i\nu_i(t_1-t_2)} \langle \hat{O}^\dagger(t') \hat{O}(t_2) \hat{O}^\dagger(t_1) \hat{O}(t) \rangle \equiv |U_i U_f|^2 N_i \int_{-\infty}^{+\infty} d(t'-t) \int_{-\infty}^{0} d(t_1-t) \int_{-\infty}^{0} d(t_2-t') e^{-i\nu_f(t-t')} e^{i\nu_i(t_1-t_2)} \langle \hat{O}^\dagger(t) \hat{O}(t_1) \hat{O}^\dagger(t_2) \hat{O}(t') \rangle$ (N_i is the population of the mode i). Utilizing the time-reversal symmetry of the molecular correlation function,[12] $\langle \hat{O}^\dagger(t) \hat{O}(t_1) \hat{O}^\dagger(t_2) \hat{O}(t') \rangle = \langle \hat{O}^\dagger(-t') \hat{O}(-t_2) \hat{O}^\dagger(-t_1) \hat{O}(-t) \rangle$, and inverting sign of the time variables yields our expression for the inverse Raman flux (see Eq. (29) of Ref. 3). We note that while the diagrams are equivalent, their form differs: the diagram (b) has the two incoming field modes on different branches, while the diagram A4 - on the same branch.

Finally, we comment on neglect of diagrams responsible for renormalization of molecular correlation functions in our considerations. For molecular junctions reasonable estimate of the interaction with the field is $U \sim 10^{-3}-10^{-2}$ eV,[13] which is negligible compared to charac-

teristic strength of molecular coupling to contacts $\Gamma \sim 0.01 - 0.1$ eV.[14] So, renormalizations due to coupling to contacts are much more pronounced. The Liouville space superoperator formulation of Ref. 1 does not handle these correlations, while the NEGF approach of Refs. 2–5 takes them into account exactly. One the other hand Ref 1 being a many-body formulation is capable of accounting for intra-molecular interactions exactly, while NEGF only allows perturbative treatment. We note that quasiparticle based Liouville formulations of Refs. 15 and 16 are similar to the NEGF in this respect. We note also, that an approach capable of both taking into account intra-molecular interactions exactly and accounting for the contacts induced renormalizations was presented in our recent publications.[17,18]

In summary, the main and the only difference between our original paper[3] and recent publication by Harbola et al.[1] is that we study specifically the Raman scattering, while paper by Harbola et al. accounts for all optical processes of the 4th order (both reducible and irreducible), and does not distinguish between different contributions to the total signal.

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