

Nonlinear signal mixing in a three-terminal molecular wire

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The authors study the electronic response of two simple molecular devices to a bichromatic field, where the device acts as a mixer. Two closely related model systems are considered: one is a benzene molecule and the other is a single grapheme sheet, and in both cases the systems are connected to three polyacetylene chains. The electronic response to the dichromatic alternating electric fields is studied by following the electron density fluctuation along the chain lengths. In both cases the electron transfer follows the field frequency at low electric fields. At higher amplitude, a significant amount of nonlinear mixing resulting in new combinations of the input frequencies is found in the spectrum. The influence of gating on the output frequencies is also shown. © 2007 American Institute of Physics. [DOI: 10.1063/1.2423023]

I. INTRODUCTION

There has been enormous interest in exploiting the quantum mechanical properties of molecules for building novel electronic devices.¹⁻⁷ Some suggested systems based on nanowires are devices with a center molecule with source and drain leads. Extensive work towards the fabrication of conducting nanowires using nanolithography techniques is under way.⁸⁻¹⁷ Due to the small size of the system, the conductance through a nanowire is ballistic. The electron phase-coherence length in ballistic conductance is on the order of or larger than the size of the system. Therefore, quantum interference may become a dominant mechanism governing the electron transport, allowing in principle the enticing prospects of *coherent electronic circuitry*.¹⁸⁻²⁴ One of the intriguing possibilities is the application of interference in building a molecular XOR gate and a molecular *resonance cavity*.²⁰⁻²³

Geometrically, a conducting nanowire is a two-terminal device, where a current between the source and the drain is controlled by the bias and, usually, by a dc gate voltage. A more general idea, which could be called ac gating, has been proposed recently—it was shown that application of a monochromatic field can dramatically affect the conductance of molecules.²⁵⁻²⁸ One of the first experimental discoveries that an external field drastically changes the usual two-terminal conductance pattern has been, for example, in multi-quantum-well heterostructures,²⁹ making further studies of ac gating very tempting. ac gating is usually brought about by exposing the molecule to a strong laser field.

An interesting point in such systems is that the nonlinear mixing between the signal and the ac gating appears even if there is no intrinsic nonlinearity in the system. When an electron moves along a system under a strong ac gating, the energy of the electron is not conserved. The electron may inductively absorb and/or emit a quantum (or several quanta) of the classical ac-gating field.²⁶ Therefore, even in linear systems, the electron energy (Floquet energy) is determined only modulo ω_g , the frequency of the gating field.

In this paper we analyze two analogous systems where nonlinear mixing takes place. We consider organic π con-

jugated materials as our mixer because of their promising potential.^{30,31} Recent studies have focused on exploiting the quantum nature of graphene molecules as a basis for coherent electronic devices.^{1,30-36} These materials are increasingly practical due to the invention of novel means of preparation.³⁷⁻⁴² In addition, graphene sheets are interesting materials due to their ferromagnetism,⁴³⁻⁴⁷ interaction with hydrogen atoms and hydrogen molecules,⁴⁸⁻⁵⁷ as well as their utility for studying fundamental physical phenomena such as the Hall effect and Berry's phase.^{58,59} The systems we consider are a benzene molecule and its larger polycyclic conjugated analog, a graphite sheet (graphene). In our signal mixing setup, they are both connected to three polyacetylene leads (Figs. 1 and 2). Interference effects in dc transport in a similar system with benzene embedded in a polyacetylene chain were first studied by Joachim and co-workers.^{60,61} In our case, however, we study a three-terminal device. Two of the polyacetylene leads serve as input leads and the third one as an output. Two monochromatic signals with different frequencies are applied on the inputs, and the output lead is followed.

Note that since our study uses a finite system without absorbing potentials or complex self-energies, the label "lead" is a little misleading and is used only for convenience, as we do not simulate an infinite lead. Physically the present simulation is qualitatively acceptable since the leads we will use are sufficiently large that the electrons have no time to transverse the whole system within an electric field oscillation even at the lower frequencies we use, so they go back and forth in a limited region. We verified, in unpublished simulations, that the results remain qualitatively the same even when we changed the system size, and in future studies we will incorporate outgoing boundary effects.

In analogy to the ac-gating problem, the conductance in our system could be viewed as conductance from one of the sources to the drain under an ac-gating coming from the other source. However, here is the subtle difference from the usual ac-gating problem. The two input leads, to which external fields (voltages) are applied, serve both as the gates

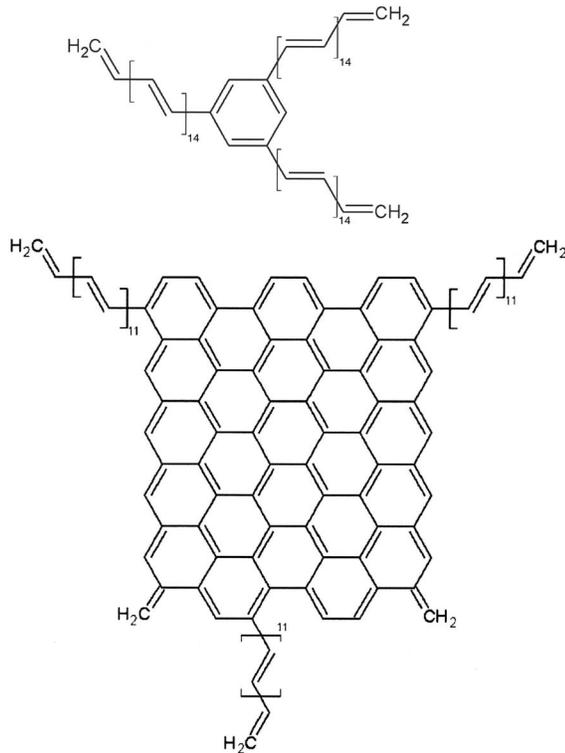


FIG. 1. (Top) The first model system studied. The system consists of a benzene molecule linked symmetrically to polyacetylene chains. Two signals at different frequencies are applied to two of the input leads. The population in the third lead is the output signal. (Bottom) The second model system studied. The system consists of graphite sheet linked to polyacetylene chains. Two voltages at different frequencies are applied to two of the input leads. The population in the third lead is the output signal.

and the sources. One cannot tell one from the other because both of them carry current in the system. They are equivalent. Therefore, this system acts more like a molecular signal mixer rather than a gated conducting molecular nanowire.

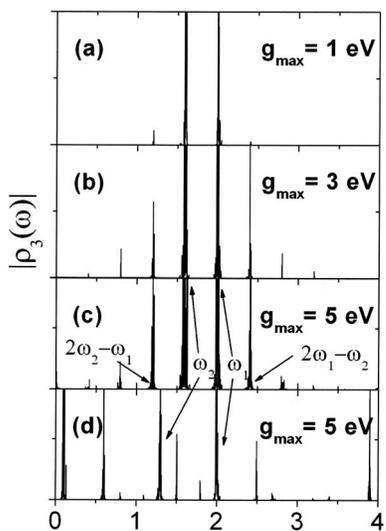


FIG. 2. The response spectra for various frequencies and field strengths. [(a)–(c)] Mixing frequencies of $\omega_1=2$ eV/ \hbar and $\omega_2=1.6$ eV/ \hbar for $g_{\max}=1, 3, 5$ eV, respectively. (d) Response spectrum at a high field strength but with different initial frequencies ($\omega_1=2$ eV/ \hbar , $\omega_2=1.3$ eV/ \hbar). The mixing in (d) is much stronger than the mixing in (c), since the frequencies sample different resonances of the Hamiltonian. Note that each plot has $|\rho_3(\omega)|$ scaled relative to its value at the input frequencies.

While we consider two-dimensional organic π systems here, the setup could consist of any molecule and three molecular leads (or even a smaller number of leads if a single lead carries both source signals). For the nonlinear effects to be sufficiently strong for observation, the frequencies of the applied signals should be of the order of the interorbital transitions in the molecule, i.e., circa an eV. The only source of such high-frequency signal, at least until recently, is a laser radiation, either from a large source or from a tip. The sub-wavelength spatial separation of the two input leads can be an obstacle for applying two different signals to the system. This could be overcome, for example, by using a near-field microscope. Another way to bypass the difficulty of the sub-wavelength size of the system is to alter the spectroscopic properties of two input leads through chemical doping⁶² or attachment of side chains with light-absorbing chemical functional groups. In such a case there will be no need for spatial resolution of the input signals.

Additionally, we investigate the effects of gating, if any, on the output of the wave-mixing process. It was demonstrated recently that it is possible to apply a gate potential to graphene sheets.⁵⁹ Despite the simple description of the electronic structure, we would like to see if it is possible to modulate the output frequencies by applying gating to specific regions of the molecule. The extended structure of the graphene surface offers a natural setting for studying the effects of a local potential shift.

In Sec. II we describe the methods used. The numerical results obtained are discussed in Sec. III, followed by conclusions in Sec. IV.

II. MODEL AND METHODOLOGY

Several assumptions have been made in our study. Most importantly, relaxation of the molecule-lead system is neglected. The model ignores scattering between electrons and atoms due to nuclear vibrations. This simplification is justified at low temperatures for rigid systems.^{2,63} The alternation of bond lengths in the polyacetylene leads (Peierls transition) is also neglected.

The Hückel or a tight-binding Hamiltonian provides the simplest one-electron picture of the molecule and the leads. All operators are in the basis of the p_z atomic orbitals of the carbon atoms. The matrix elements of the Hückel Hamiltonian are commonly parametrized as follows:

$$\mathbf{H}_{\text{Hückel}}(i,j) = \begin{cases} \alpha & \text{if orbitals } i=j \\ \beta & \text{if orbitals } i,j \text{ are on nearest neighbors} \\ 0 & \text{otherwise,} \end{cases} \quad (1)$$

where we used optimized parameters for π conjugated molecules.⁶⁴ For aromatic molecules such as polycyclic aromatic hydrocarbons (benzene) and polyacetylenes, $\alpha=-6.6$ eV and $\beta=-2.7$ eV are used.⁶⁵ Although the Hückel model is a one-electron picture, it has been used to yield qualitatively correct predictions for the polycyclic aromatic hydrocarbons we are studying here.^{22,66}

The presence of a gating potential conceivably shifts the energies of the atomic orbitals. As a result, the gating effect

is most simply incorporated by adding to the parameter α a constant so that $\alpha \rightarrow \alpha + \Delta$, and we chose here $\Delta = 2.0$ eV for orbitals on atoms within the regions affected by the gate. Two gating regions, each covering a hexagon on the graphene surface, are selected for studying the gating effect.

By the linear variational principle, the molecular orbitals and their energies are the eigenvectors and eigenvalues of the equation⁶⁷

$$\mathbf{H}_{\text{Hückel}}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}. \quad (2)$$

The matrix \mathbf{S} is the overlap matrix which is assumed here to be the identity matrix. \mathbf{C} is the matrix of the eigenvectors of the matrix $\mathbf{H}_{\text{Hückel}}$. Each column of \mathbf{C} contains the coefficients that define an eigenvector in terms of the atomic orbital basis.

In our calculations we assume that initially no external potentials were applied to source leads. Since initially the total Hamiltonian is equal to the Hückel portion only, the initial density matrix ρ is obtained from

$$\rho(t=0)_{ij} = \sum_k^L \mathbf{C}_{ik}\mathbf{C}_{jk}^*, \quad (3)$$

where L is the number of occupied orbitals.

At later times, two external potential pulses are applied to the source leads. To distinguish between the leads we enumerate them such that leads one and two are the source leads and lead three is the drain. The total Hamiltonian including the influence of the external potentials has the following form:

$$\begin{aligned} \mathbf{H} &= \mathbf{H}_{\text{Hückel}} + \mathbf{H}_1 + \mathbf{H}_2, \\ \mathbf{H}_1(i, i) &= f(t)\sin(\omega_1 t)g_1(i), \end{aligned} \quad (4)$$

$$\mathbf{H}_2(i, i) = f(t)\sin(\omega_2 t)g_2(i).$$

Here, ω_1 and ω_2 are the frequencies of the applied potentials and $f(t)$ is a smooth function of time which is necessary to avoid unnecessary high-frequency harmonics generation due to a swift external potential switch on. We chose $f(t)$ to be of the following form:

$$f(t) = 1 - e^{-at^2}, \quad (5)$$

where the parameter a defines the smoothness of the switching of the external potentials. We used $a = 0.1$ (eV/ \hbar)², which corresponds to a switching time of $t_{\text{switch}} = a^{-1/2} \approx 2 \times 10^{-15}$ s.

The dependence of the external potential coefficients $g_1(i)$ and $g_2(i)$ on the site index i reflects the real-space finiteness of the external potentials applied to the source leads. They should be defined so that they are approximately of unit magnitude for atomic orbitals near the centers of the first and second leads ($j_{\text{center},1}, j_{\text{center},2}$) and smoothly fall off as they approach the central part of the system. We chose the following form for the coefficients:

$$g_1(j) = \begin{cases} g_{\text{max}}/(1 + e^{(j-j_{\text{center},1})/4}) & j \text{ on lead "1"} \\ 0 & \text{otherwise,} \end{cases} \quad (6)$$

where we took $j_{\text{center},1} = 23$. An analogous definition is used for g_2 for the second lead.

It is important to note that the electric field influences here the energies through a shift of the molecular energies, rather than the more usual approach whereby an electric field is coupled to the dipole moment. The reason for this is that physically, the system, except at high frequencies, will be polarized so that the potential drop off will occur mostly on and near the molecule and the potential on the leads will be of approximately constant spatial extent. Since the Hamiltonian we use here has no polarization, we put by hand the effect of the electric field as a shift in the diagonal energies rather than using the bare electric field with a dipole. This picture will be more valid at the lower frequencies we consider (frequencies below 1 eV/ \hbar , see below) and less valid at the higher energies. While properly one needs to include polarization effects and to simulate with a bare electric field, the qualitative effects of the mixing should be valid even for this simplistic Hückel calculation.

The density matrix evolves with time according to the Liouvillian equation of motion:⁶⁸

$$\left(\frac{d\rho}{dt}\right) = -\frac{i}{\hbar}(\mathbf{H}_{\text{tot}}\rho - \rho\mathbf{H}_{\text{tot}}). \quad (7)$$

A fourth-order Runge-Kutta⁶⁹ method was used to propagate the elements of the density matrix. A time step of 0.05 (eV/ \hbar)⁻¹ (corresponding to about 30 as) was sufficient for convergence of the population results.

We used a Mulliken approach to measure populations in the leads.⁶⁵ The population on, say, the third lead (the drain lead) is the sum over the diagonal elements of the density matrix corresponding to the atomic orbitals that describe the lead:

$$\rho_3(t) = \sum_i^{\text{lead 3}} \sum_j^{\text{O}} \rho_{ij}(t)\mathbf{S}_{ji}. \quad (8)$$

The electron density on the third lead as a function of time is the primary quantity we calculate. To demonstrate the effect of the nonlinear frequency mixing we plot the spectrum of drain population,

$$\rho_3(\omega) = \int \rho_3(t)e^{-i\omega t} dt. \quad (9)$$

III. RESULTS AND DISCUSSION

The response spectra of benzene for the first set of input frequencies at $\omega_1, \omega_2 = 2, 1.6$ eV/ \hbar (as well as $2, 1.3$ eV/ \hbar) and for the second set at $\omega_1, \omega_2 = 0.2, 0.16$ eV/ \hbar are given in Fig. 2 and 3. The response spectra of the graphene molecule for $\omega_1, \omega_2 = 2, 1.6$ eV/ \hbar are given in Fig. 4.

In general, in a nonlinear mixing process of two input waves the output spectrum should consist of peaks at frequencies which are all the possible linear combinations of the input frequencies:

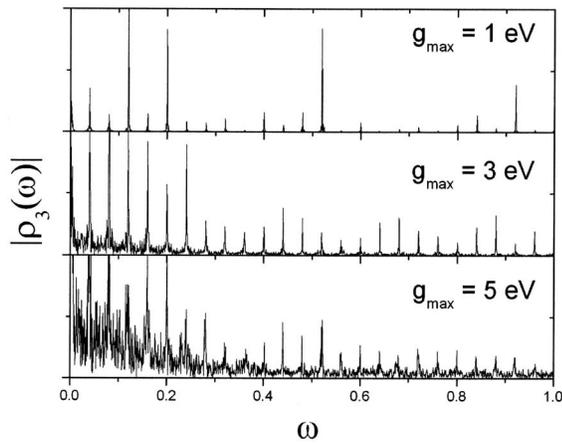


FIG. 3. Response spectra of a connected benzene model for lower frequencies $\omega_1=0.2$ eV/ \hbar and $\omega_2=0.16$ eV/ \hbar at $g_{\max}=1,3,5$ eV, respectively. Each plot has $|\rho_3(\omega)|$ scaled relative to its value at the input frequencies.

$$\omega = l_1\omega_1 + l_2\omega_2, \quad l_{1,2} = 0, \pm 1, \pm 2 \dots$$

The positions of the peaks on the frequency scale are fixed, so that the form of the output spectrum is uniquely determined by the relative heights of all the peaks. The form of the spectrum changes as the input intensities change.

There are two asymptotic limits of the response spectrum: the linear and highly nonlinear regimes. The linear regime corresponds to weak inputs. This regime is characterized numerically by a small parameter $\alpha = \kappa V \ll 1$, where κ is a characteristic constant describing the nonlinear wave generation in the specific system and V is the quantity proportional to the input strength. The intensity of the processes drops as αV^N , where N is the order of the process.

At weak fields the dominant contributions to the response spectrum are given by linear processes, $N=1$. This is seen in Fig. 3, where the response spectra of benzene for the two sets of input frequencies, $\omega_1=2$ eV/ \hbar , $\omega_2=1.6$ eV/ \hbar and $\omega_1=2$ eV/ \hbar , $\omega_2=1.3$ eV/ \hbar , are given at several input strengths up to $g_{\max}=5$ eV. At $g_{\max}=1$ eV, only the linear response peaks at the input frequencies $\pm\omega_1$ and $\pm\omega_2$ are present. However, with higher input strengths $g_{\max}=3$ and 5 eV the peaks corresponding to the nonlinear wave-mixing start appearing, e.g., the peaks with frequencies $2\omega_1 - \omega_2$ and

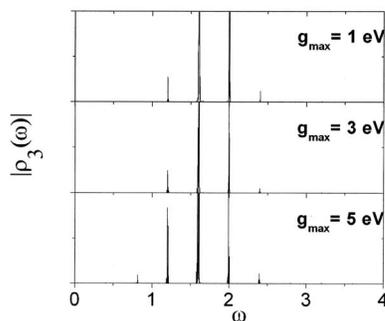


FIG. 4. Response spectra of the graphene model, with $\omega_1=2$ eV/ \hbar and $\omega_2=1.6$ eV/ \hbar at $g_{\max}=1,3,5$ eV, respectively. Each plot has $|\rho_3(\omega)|$ normalized relative to its values at the input frequencies. Note that mixing at higher values of g_{\max} leads to significantly larger output (relative to the input).

$2\omega_2 - \omega_1$ as indicated in the figure. At $g_{\max}=3$ eV the mixer is in an intermediate region ($\alpha=1$), at which higher order peaks start appearing.

Interestingly, the resulting spectra are strongly dependent on the mixed frequencies. Figures 2(c) and 2(d) show that for the same input voltage, and the same input frequency on lead 1, the nonlinear response is much weaker if $\omega_2=1.6$ eV/ \hbar than for $\omega_2=1.3$ eV/ \hbar . This is due to differences in the resonances sampled by the two frequencies.

The nonlinear signal strength dependence is seen in the graphene model (Fig. 4). The mixing effect in our graphene model is smaller than for benzene but similar. It remains to be seen whether interference effects can be enhanced in similar graphene models with slightly altered conjugated π bonding, an effect previously demonstrated computationally.²¹

In the opposite regime of a highly nonlinear response the form of the spectrum depends on the input frequency commensurability. At this regime, all the possible peaks in the spectrum are present. If the input frequencies are commensurate, i.e., $\omega_1=k_1\Delta$, $\omega_2=k_2\Delta$, with some integers k_1 and k_2 , then the spectrum looks as a series of peaks at frequencies $\omega=K\Delta$, $K=0, \pm 1, \pm 2, \dots$. In the case of incommensurate input frequencies the spectrum should be continuous. The commensurability parameters for the two pairs of the frequencies considered in the linear response regime are 0.4 and 0.1 eV/ \hbar , respectively. Therefore, at the highly nonlinear regime the first set, $\omega_1=2$ eV/ \hbar , $\omega_2=1.6$ eV/ \hbar , is preferable for observing the structure of the response spectrum. The response spectra of benzene at $g_{\max}=3$ and 5 eV are given in Figs. 3(b) and 3(c), respectively. In reality, the highly nonlinear response regime is not reached here so only low order nonlinear processes reveal themselves. In this sense the commensurability is not an issue for real systems.

As mentioned above, we also studied the effects of gating on output of the mixing process. The gating potential is applied to two regions on the graphene sheet, as depicted in Fig. 5. The response spectra of graphene with and without gating are given in Fig. 6. The results show that the application of the gating potential alters the output of the mixing process substantially.

It is interesting to speculate on the origin of the change in the response with gating. Physically, this may have to do with the high symmetry and large extent of the graphene model without the gating. The symmetry may prevent some higher order harmonics due to destructive interference, so by breaking it new frequencies appear. A simpler (but related) explanation is that by introducing the gating, we introduce smaller length scales to the problem, since the electrons may now reflect after traveling shorter distances. These smaller length scales and the abrupt changes in the potentials due to gating lead to the incorporation of higher harmonic mixing, which broadens the overall spectrum.

IV. CONCLUSIONS

We propose here that organic π conjugated materials can be used as a simple tool, mixer, in coherent ac electronic circuitry. In particular, we used a simple electronic structure method to demonstrate numerically that such materials could

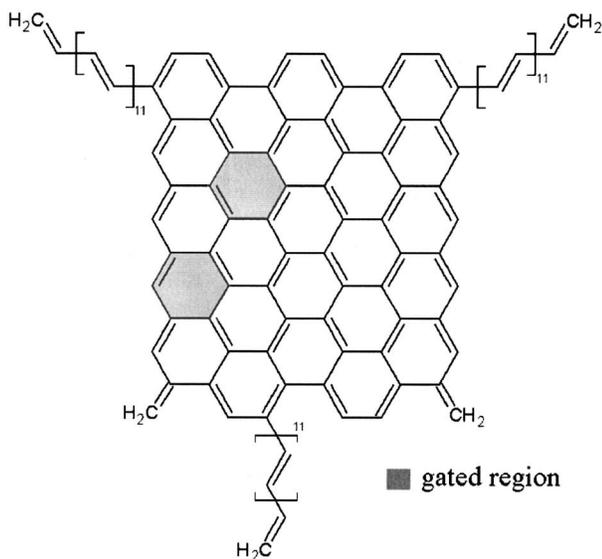


FIG. 5. The shaded areas indicate the regions where the gating potential is applied on the graphene sheet. The atomic orbitals on the six carbon atoms bordering each shaded region are affected by the gating. The gating effect on the electron dynamics is incorporated as explained in Sec. II.

act as a wave mixer. The two leads in this three-terminal device act as inputs and the third lead provides the output signal. Further, numerical results suggest that gating can be used to control the output of the mixing process. This idea is not so far fetched as others have pointed out the quantum nature of two-dimensional graphene systems allow them to be electronic waveguides.³⁶

To be ever used as a true mixer the response spectrum of the device needs to be improved so that one or a few frequencies are chosen. For this purpose, rigid molecules such as nanotubes could conceivably be used. A practical device will most likely use a system where the response of the molecule is resonant in a specific mixing frequency, or where interference effects increase the response of a few harmonics and reduce the effects of others.

In practice, the calculations here are very similar to that of a Raman spectrum for a nonlinear driving. However, this does not mean that the systems considered are associated with a purely optical response of a single molecule. Such a

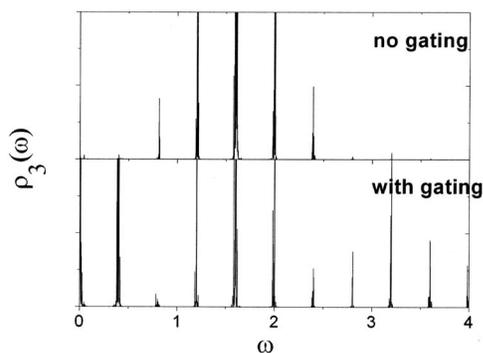


FIG. 6. (Top) The response spectrum of the graphite model without gating with $\omega_1=2$ eV/ \hbar , $\omega_2=1.6$ eV/ \hbar , and $g_{\max}=5$ eV. (Bottom) The response spectrum for the gated system as illustrated in Fig. 5, for the same driving frequencies and electric field amplitude. Each plot has $|\rho_3(\omega)|$ scaled relative to its value at the input frequencies.

circuit can be attached coherently to several other circuits to yield a purely electronic ac circuit which can be driven, and presumably read, optically, but acts electronically; this is of course a very long term prospect.

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