Ballistic photocurrent driven by optical phonon modes in a polaronic ferroelectric

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(Dated: August 23, 2022)

We investigate the effect of local electron-phonon coupling on nonlinear optical conductivity in an interacting ferroelectric system. Using real-time simulations, we show an enhancement in nonlinear conductivity under linearly-polarized light due to generation of the phonon-assisted ballistic-current in addition to the injection-current generated by electron-hole pairs. The optically excited phonon modes generate an asymmetric carrier distribution that causes a strong directional ballistic-current. The ballistic-current enhances the photocurrent several times at above band-gap excitation frequencies and is sublinearly dependent on the excitation intensity. This strong phonon-assisted zero-frequency directional ballistic-current demonstrates an alternative way to boost the bulk photovoltaic effect (BPVE) in electronic ferroelectric materials with strong local el-ph coupling.

The nonlinear optical effects in quantum materials have been extensively studied due to their strong fundamental and technological relevance [1, 2]. For example, the coupling between the polarization and optical properties in solids lacking inversion symmetry, such as ferroelectrics, causes unconventional photo voltaic effects, known as bulk photovoltaic effect (BPVE) [3, 4]. The BPVE is the generation of directional (dc) photocurrent due to above-bandgap electronic excitations under an external electric field [3, 5].

The dc-current generated in BPVE can be classified into two types: shift-current and ballistic-current [6–8]. The shift-current is a purely coherent quantum phenomenon that involves the relative shift of the electron cloud in real space during excitation under linearly-polarized light. It is independent of any scattering mechanism, and its relaxation occurs at electronic timescales. On the other hand, the ballistic-current (also referred to as injection current) arises from the asymmetric momentum distribution of carriers due to scattering processes such as electron-phonon (el-ph) [4, 6, 9–12], electron-electron (el-el) [13], and electron-spin (el-s) scattering. Another form of injection current is present under circularly polarized light, where population asymmetry is generated by photoexcitation instead of scattering [14]. Higher-order photocurrents which involve population asymmetry depend on various kinetic processes that span a range of time scales [15, 16], unlike the coherent shift current process.

While past theoretical studies of the BPVE have mostly been performed in perturbation theory, recent works have shown that naive application of perturbation theory can lead to incorrect results for the shift and injection currents in certain limits [17]. Furthermore, the use of the independent-particle approximation in the frozen band picture limits the predictive power of such studies in non-perturbation regions [13]. Dynamical effects, such as carrier momentum and energy relaxation due to elastic and inelastic scattering, are known to significantly affect the BPVE properties of materials [13, 17–19]. The rate of relaxation of energy and momentum depends on the interactions el-ph, el-el, and el-s and impurities, all of which are intrinsic properties of materials [20, 21]. In addition to carrier scattering, quasi-particle effects, such as excitonic dynamics, are also known to affect photocurrent dynamics and produce a non-trivial photovoltaic response [13, 17–19].

The phonon-induced ballistic current has only been treated within perturbation theory in previous studies [9, 22]. With the limitations of perturbation theory for shift and injection currents in mind, we reexamine the phonon-induced ballistic current using nonperturbative real-time simulations in the present study. We demonstrate that a phonon-induced ballistic current can be sustained at steady state, using a one-dimensional polaronic ferroelectric system as an illustrative model. Importantly, local el-ph coupling (of the Holstein-type) favors the generation of this photocurrent. These optical phonon modes coupled to charge-transfer electronic excitations cause strong asymmetric el-ph scattering that generates a ballistic photocurrent. This phonon-assisted current is unidirectional, and results in a strong BPVE response independent of light polarization. The magnitude of the reported ballistic-current originating from optical phonon modes is the largest contributor to the BPVE in this system. We observe a departure from the predictions perturbation theory in the high intensity limit. Our reported large contribution of the ballistic-current to BPVE originating from phonon dynamics can explain the temperature dependence of the photocurrent, which cannot be resolved by the shift current theory, recently observed in the ferroelectric organic molecular system [23].

Our study suggests possibilities for strengthening the nonlinear optical rectification and the BPVE effect in ferroelectrics with strong el-ph interactions displaying bound excitations and long-lived optically excited high-frequency phonon modes, such as complex transition-metal oxides or charge-transfer organic salts.

We consider a minimal one-dimensional ferroelectric
model with an el-ph interaction. Motivated by three-dimensional ABO$_3$ transition-metal perovskite oxides, the model consists of a chain of corner connected BO$_6$-octahedra with the z-axis along the chain. The Hilbert space consists of a single electron orbital on each B-type ion. Electronic hopping between these B-type orbitals is mediated via intermediate O-type sites, similar to transition metal oxides. These electrons are described by one-particle wavefunctions where each wave function is a two-component spinor. The wavefunctions are expressed in terms of local spin-orbital wavefunctions.

The first and second terms correspond to the electron hopping between B-sites and the el-ph interaction, respectively. $t_{hop}$ and $g$ are the strengths of the hopping and el-ph coupling. For every $j^{th}$ B-site, we consider the local octahedral breathing mode $Q_j$, defined as $Q_j = \frac{1}{\sqrt{3}}(d_{x^2-y^2} + d_{y^2-z^2} + d_{z^2-x^2})$ where $d_{x^2-y^2, i}$ is the distance between O-type ions forming octahedra around the $i^{th}$ B-site along $x/y/z$ direction and $d = 3.85$ Å is the equilibrium O-O distance. These $Q_j$ modes are coupled to the electron density at the respective $j^{th}$ B-sites. The third term in $E_{pot}$ is the potential energy of the displacements of $u_j$, where $K$ is the restoring force constant.

The restoring force constant $K$ is related to the mass $M_O$ and the vibration frequency of the phonon mode $Q_j$ by $K = M_O \omega_j^2$. We fix $K = 10$ eV/Å$^2$ so that the vibration frequency of the $Q_j$ modes, assuming $M_O$ as the mass of oxygen atoms, is in the range of the frequencies of optical phonon modes such as Jahn-Teller and breathing modes, in transition-metal oxides.

Finally, we include local el-el interactions via the $U$ parameter. This term incorporates a fast decoherence and relaxation effect within the electronic subsystem. These effects are present in most materials, and serve to bring the system to a steady state under photoexcitation.

We calculate the ground state phase diagram of the model, defined in Eqn. 1, at half-filling (one electron per BO$_6$-site) as a function of the model parameters $(g, \delta)$, with the phononic $(Q)$ and electronic $(\psi)$ degrees of freedom allowed to relax to their lowest energy configuration. Finite $Q_j$ modes act as an onsite potential $\Delta_j^B = gQ_j$ for electrons. For $U = 0$, the ground-state exhibits an insulating phase with a charge density wave (CDW) for $g > g_c$. The CDW is accompanied by lattice distortions reflected in finite $Q_j$ modes. An increase in the onsite $U$ drives the system toward the spin density wave (SDW).
binding energies measured in hole-doped transition-metal oxides are in the range of 100-500 meV [26]. In our current 1-d model, the range of parameters $g_{fr}$ = 2.50–3.50 eV/Å and $\delta$ = 0 – 0.05 eV reproduces a similar $E_b$.

To simulate the real-time dynamics of photocurrent generation and its evolution under a light field, we employ Ehrenfest dynamics. The one-particle electron wavefunctions evolve under the time-dependent Schrödinger equation, while the atoms obey the classical equations of motion.

The effect of the linearly polarized light field, defined by the vector field $\vec{A} = (A_o e^{i\omega_o t} + A_o e^{-i\omega_o t}) \vec{e}_z$, where $A_o$ is the amplitude of the vector potential and $\hbar\omega_o$ is the photon energy, is incorporated into the model 1 using the Peierls substitution method [27].

For the real-time simulations of the BPVE, we consider the polaronic ferroelectric state as the initial state with band-gap $E_{gap} = 0.411$ eV at time $t=0$. In the initial state, the chain is dimerized with a staggered pattern of local distortion $Q_1$, and with zero initial velocities. The BPVE effect is investigated in the parameter ranges $\delta = 0.0 – 0.025$ eV and $g = 2.75 – 3.0$ eV/Å while keeping $\hbar\omega_1 = 0.50$ eV and $U = 0.50$ eV fixed.

The simulations are carried out with a time step $dt = 0.96 \times 10^{-17}$ s in a supercell with 4 A-type sites and periodic boundary conditions. We used a $N_k = 800$ point k-grid symmetric around the $\Gamma$-point. Firstly, we investigate the spectral distribution the photon absorption density $D_p = \delta E_{f-1}/\hbar\omega$, where $\delta E_{f-1}$ is a change in $E_{tot} = E_{kin} + E_{pot}$, before and after a short 20-femtosecond Gaussian-shaped light pulse. The system shows a broad absorption peak with a band-gap of 0.411 eV, see Figure 1-c.

Next, we consider the effect of a continuous-wave light field on the photocurrent. Figures 1-d shows the spectrum of the time integrated-current $\int j^{tot}(t) dt$. where the total current $j^{tot}(t)$ is defined as

$$j^{tot}(t) = \sum_{n} f_n \sum_{j} e^{i\vec{A}(t) \cdot \vec{d}} (t_{hop} + (-1)^j \delta) \left( \psi_{j,n}(t) \psi_{j+1,n}(t) - \psi_{j+1,n}(t) \psi_{j,n}(t) \right) \vec{e}_z. \quad (2)$$

The current is integrated over a period $t_f = 1.08$ ps to $t_f = 1.45$ ps. In the presence of atom dynamics, the system displays a strong photocurrent over a wide energy range between $\hbar\omega = 0.40–0.60$ eV. We attribute this photocurrent to ballistic-current $j^{ballistic}(t)$ generated as a result of asymmetric carrier scattering by phonon modes. In comparison, the photocurrent in the frozen-atom case is several times smaller. We attribute this contribution to the photocurrent to injection current induced by electron-hole (el-h) pair creation under linearly polarized light as discussed in Ref. [13].

In figures 2 and 3, we show the evolution of the total photocurrent and carrier populations as a function of time at three different excitation frequencies $\hbar\omega_p$. In the beginning, the dynamics is highly non-equilibrium in nature, with a continuous increase in the photocurrent, excited-state populations and total energy $E_{tot} = E_{kin} + E_{pot}$ of the system, where $E_{kin}$ is the kinetic energy of atoms. For excitation at $\omega_p$, the system reaches quasi steady-state at time $t \sim 1.0$ ps, which is reflected in the saturation of the photocurrent, excited state populations, and total energies. The time taken to reach steady state increases as the excitation frequency is increased to $\omega_p$ and $\omega_p$. The correlation between the saturation of the photocurrent with the saturation of the carrier populations is consistent with the photocurrent being mostly ballistic current, which is sensitive to the carrier populations.

Optical excitations from the valence band to the conduction band in the polaronic ferroelectric state are accompanied by charge-transfer between sites, altering local charge densities $\rho_i(t)$. The phonon modes $Q_i(t)$ are coupled with local change densities $\rho_i(t)$. Thus, changes in $\rho_i(t)$ induce atomic displacements, which are primarily high-frequency optical phonon modes, as seen in Figures 3-b.

Bulk photocurrents arise in the scattering picture [28] when carriers occupy an asymmetric carrier momentum distribution $\tilde{f}_{m,k} \neq \tilde{f}_{m,-k}$ in the Brillouin zone. This asymmetric carrier momentum distribution can be induced by scattering from phonons or el-h pairs. Thus, the sum $j^{scattering}(t)$ of the ballistic- and injection-current induced by el-ph and el-hole scattering is

$$j^{scattering}(t) = j^{ballistic}(t) + j^{inj}(t) = -e \sum_{k,m} \tilde{f}_{m}(k,t) v_{m}(k,t) \quad (3)$$

where $\tilde{f}_{m}(k,t)$ and $v_{m}(k,t)$ are the momentum distribution and the electron velocity in band $m$, respectively. For the present two-band model, the electron velocities
that the shift current, which constitutes the shift current, is understood to be the shift current. In this one-dimensional polaronic ferroelectric insulator, populations arise from carrier coherences instead of carrier populations [8], is understood to be the shift current. We find that most of the photocurrent in this system of the model forbids asymmetric band velocities. Asymmetric occupations because time-reversal symmetry eration of ballistic and injection currents is entirely due to asymmetric occupations that arise from carrier coherences instead of carrier populations [8].

Now we consider the effect of the el-ph coupling parameter $g$ and the hopping asymmetry $\delta$ on the current. Figure 4-b shows the total current $\int j_{\text{tot}}(t)dt$ for four different el-ph coupling strengths. Even though some amount of el-ph coupling is necessary to create an asymmetric carrier distribution, a larger value of el-ph coupling does not always result in larger ballistic current. For this range of parameters, we observe that $\int j_{\text{tot}}(t)dt$ decreases with increasing $g_{bo}$ close to the band edge, but...
has the opposite trend away from the band edge. This is because besides asymmetric carrier scattering rate, the carrier velocities have a significant impact on the ballistic current (Eq. 3). The renormalization of the carrier velocities near the band edge is reflected in the higher band edge $\int J^\text{tot}(t) dt$ at $g = 2.80$ eV/Å compared to $g = 3.00$ eV/Å and 3.10 eV/Å.

The model parameter $\delta$, see Eqn. 1, describes the relative asymmetry between the bands. A higher value of $\delta$ means greater asymmetry between the bands. Changing $\delta$ from 0.00625 eV to 0.0125 and 0.025 eV (Figure 4-c) enhances the current almost by a factor of two and four, respectively. This shows that a higher $\delta$ generates a stronger BPVE. This is similar to the behavior of the shift-current, which also increases with $\delta$.

Our present study highlights the importance of optical phonon modes and the polaronic effect in inducing a strong photocurrent in ferroelectric insulators. We show that Holstein-type el-ph coupling produces strong zero-frequency ballistic-current. Multiferroic oxides and charge-transfer organic salts are potential candidates for the realization of strong BPVE. In multiferroic oxides, ferroelectricity originates from the underlying charge and orbital order that are strongly coupled to local atomic distortions, and the band gap is sensitive to these distortions [19, 21]. The d-d-type electronic transitions across the bandgap in such systems are expected to generate a strong non-linear photovoltaic response.

Using a tight-binding model with realistic parameters, we have shown that phonon-induced ballistic current can be supported in a polaronic ferroelectric, and it can be the dominant contributor to the bulk photocurrent when the right form of el-ph coupling is present. The high-frequency phonon modes that are coupled to electronic excitations generate an asymmetric momentum distribution of charge carriers and induce a strong directional ballistic photocurrent. Our study suggests that the effects of optical phonon modes strongly influence the BPVE properties, and understanding the contribution of these effects is essential to boost the bulk photovoltaic response in ferroelectrics known to exhibit polaronic character.

S.R., T.O., and L.Z.T were supported by the Computational Materials Sciences Program funded by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Additional support for absorption calculations was obtained from the Molecular Foundry, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.
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