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Quantum interference between the optical Stark effect and resonant harmonic generation in WS_2

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An applied field can modulate optical signals by resonance shifting via the Stark effect. The optical Stark effect uses ultrafast light in the transparency region of a material to shift resonances with speeds limited by the pulse duration or system coherence. In this Letter we investigate the optical Stark effect in resonant optical harmonic generation using the A exciton transition of WS_2. Multidimensional pump-harmonic-probe measurements, in which the probe is second- or third-harmonic emission, reveal not only large Stark shifts that are commensurate with the large optical susceptibilities common to WS_2 excitons, but also behaviors more complex than simple optical Stark effect treatments predict. We show how a new manifestation of the Stark Effect, brought forth by coherent photon exchange between the pump and harmonic generation fundamental fields, can strongly enhance or suppress harmonic generation.

Optical harmonic generation (OHG) is an important light generation mechanism and a ubiquitous probe in microscopic analysis. Harmonic generation occurs when a strong light field, E, of frequency ω, drives a non-linear polarization that coherently radiates new light fields at the harmonics of the original frequency, $\{2\omega, 3\omega, \dots\}$ (Figure 1a).[1, 2] Optical harmonic generation spectroscopy is sensitive to applied fields,[3–6] and is a selective probe of semiconductor materials in ways complementary to that of traditional absorption and reflection probes.[5, 7–9]

A related optical process, also requiring strong light fields, is the optical Stark effect (OSE). In the optical Stark effect, a non-resonant optical pump creates photon-dressed states that hybridize with the system's original eigenstates, shifting their energies (Figure 1b) by:

$$\Delta E = \frac{\left|\mu_{ab}\right|^2 \mathcal{E}_{\text{pump}}^2}{E_0 - \hbar\omega_{\text{pump}}}, \tag{1}$$

in which $\mathcal{E}_{\text{pump}}$ is the field amplitude, μ_{ab} is the transition dipole between states a and b, and $E_0 \equiv E_b - E_a$ is the unpumped transition energy.[10–13] The optical Stark effect is well-known in semiconductor exciton systems, but it is typically probed with a weak electric field.[14–17]

The optical Stark effect can have an important interplay with optical harmonic generation. In resonant harmonic generation, the optical Stark effect alters resonance enhancement, which can modulate the harmonic generation efficiency.[18, 19] Since the OSE is adiabatic, its ultrafast control of harmonic generation may suit photonics applications like optical modulators.[20] The optical Stark effect also alters the free induction decay of the system, complicating pump-probe signals at the earliest pump-probe time delays and requiring careful attention to distinguish from absorption effects like spectral hole burning.[21–24] These potential applications and effects

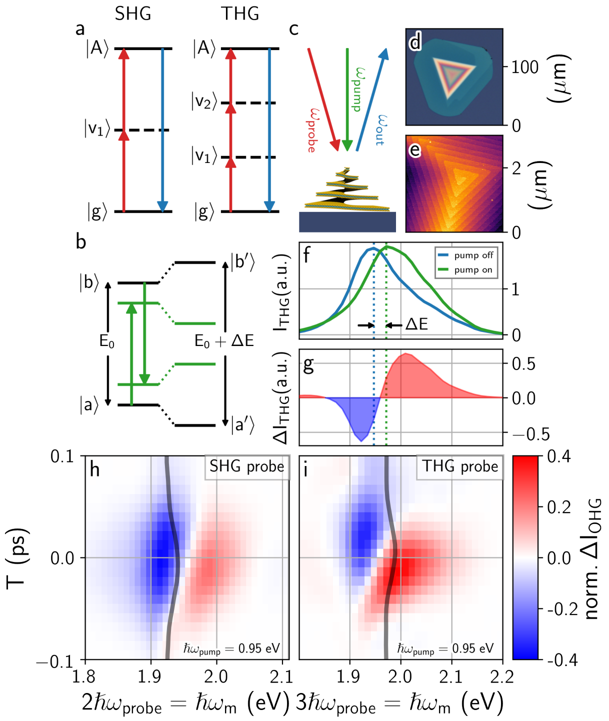

FIG. 1. Overview of the optical Stark effect and optical harmonic generation in WS_2. (a) Energy level diagrams with a probe (red) creating an A exciton coherence which then emits at a frequency (blue) which is a harmonic of the probe. (b) Non-resonant optical Stark effect in which a pump (green) drives the $a \leftrightarrow b$ transition which results in photon-dressed states with energy $E_0 + \Delta E$. (c) Illustration of the experimental geometry with $\omega_{\text{out}} = n \cdot \omega_{\text{probe}}$ and n being 2 for SHG and 3 for THG. (d, e) Optical and atomic force microscopy images of the WS_2 screw-dislocation pyramid on Si/SiO_2. (f) THG spectrum with NIR pump on and off. (g) Difference between THG spectra in (f). (h,i) Difference between unpumped and pumped OHG spectrum (h: SHG, i: THG) for different pump-probe time delays, T. The thick black lines are the center-of-mass of the pumped harmonic generation spectrum.

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motivate a study of the modification of optical harmonic generation by the optical Stark effect.

In this Letter we connect the optical Stark effect to optical harmonic generation by exploring IR pump, harmonic probe spectroscopy of WS_2. This OHG-probe spectroscopy is an example of the emerging methods which extend the capabilities of traditional pump-probe methods by using higher order interactions for the pump and/or probe.[8, 9, 25–28] It is imperative to understand how the optical Stark effect influences this spectroscopy because processes like charge separation at heterojunctions occur during pump-probe overlap.[29] The optical Stark effect and optical harmonic generation are pertinent for 2D transition metal dichalcogenides (TMDCs), where resonant optical transitions are generally strong.[7, 30–40] Herein we show that the optical Stark effect is strong for optical harmonic generation, with resonance shift rates in excess of 2 meV per $\frac{\mathrm{V}}{\mathrm{nm}}$ of applied optical field. In addition to the well-known optical Stark effect blue shift, we find the OSE-OHG process incurs novel hybridization between the pump and probe fundamental fields. When the pump and the probe fundamental have similar frequencies, quantum interference[41] of the pump and probe photons strongly modulate the efficiency of harmonic generation. By tuning the pump frequency about the probe fundamental, the interference can either greatly suppress or enhance harmonic generation. The effect is similar to the recent photocurrent modulation using the interference of different multiphoton absorption processes.[42–44]

Our experiments use two optical parametric amplifiers to generate linearly polarized pump and probe pulses ($\Delta_t \approx 50$ fs FWHM) (additional details are available in the Supplemental Material[45]). We measure second harmonic generation (SHG) or third harmonic generation (THG) of the probe beam (Figure 1c) from a single WS_2 screw-dislocation spiral (84 nm tall, Figure 1d,e) on a Si/SiO_2 substrate; we use a TMDC screw-dislocation because they are known to have excellent non-linear optical properties.[46–49] Figure 1f shows the A exciton THG resonance of the spiral (blue line). When a non-resonant pump (0.95 eV) is applied, the resonance blue-shifts (Figure 1f, green line), yielding an asymmetric difference line shape (Figure 1g).

To investigate pump-OHG-probe, we measure the harmonic generation efficiency dependence on the pump and probe frequency, relative arrival time, and fluence. We look at changes in harmonic generation intensity relative to the peak of the unpumped harmonic generation spectrum:

$$\text{norm. } \Delta I \equiv \frac{I_{\text{OHG, pumped}} - I_{\text{OHG, unpumped}}}{\max\left\{I_{\text{OHG, unpumped}}\right\}}. \tag{2}$$

Figure 1h(i) shows the pump-SHG(THG)-probe spectrum as the pump-probe delay is scanned. The thick gray line traces the center of mass of the pumped resonance at the different pump-probe time delays, T; the pump blue-shifts both SHG and THG with a time dependence that roughly follows the pump-probe temporal overlap. The baseline value of the SHG (gray line, 1.92 eV) shows that its resonances is shifted from that of the A exciton resonance. This difference in resonance frequency, along with the significantly weaker transition dipole (see the Supplemental Material[45]), suggests that the SHG resonance is not from the A exciton but perhaps a trion.[3] Henceforth we focus on THG of the A exciton.

Figure 2 shows the THG dependence on pump frequency, $\hbar\omega_{\text{pump}}$, probe frequency, $\hbar\omega_{\text{probe}}$, and pump-probe time delay, T. When the probe arrives before the pump ($T < 0$), THG is enhanced near the resonance ($\Delta I > 0$). When pulses are overlapped ($T \approx 0$), the probe spectra (horizontal slices) are dispersive, which is consistent with blue-shifting of the exciton resonance. When the probe is delayed by times greater than the pulse duration ($T > 50$ fs), response is observed only when $2\hbar\omega_{\text{pump}} > E_0$, indicating that the pump is dissipating energy via two photon absorption (2PA). The effects of absorption persist beyond 50 ps (see Figure S15 in the Supplemental Material[45]).

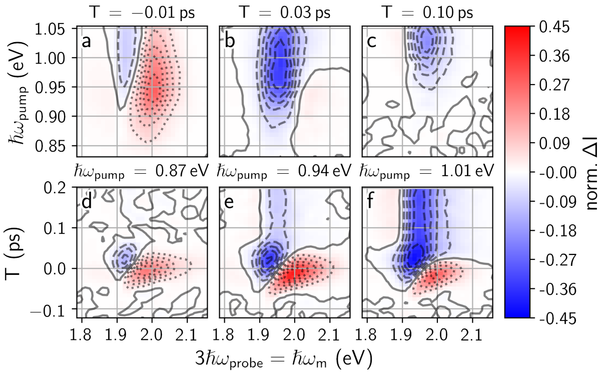

FIG. 2. Effects of pump frequency, probe frequency, and pump-probe time delay on WS_2 THG spectrum. (a-c) pump frequency vs. probe frequency for different time delays. (d-f) time delay vs. probe frequency for different pump frequencies. The colormap is shared across all panels with contour lines locally normalized. $\mathcal{F}_{\text{pump}} \approx 3000 \frac{\mu\text{J}}{\text{cm}^2}$.

Significantly, some of the pump-OHG-probe behaviors shown in Figure 2 run counter to expectations from the conventional optical Stark effect. For example, the probe line shapes (horizontal slices of Figure 2) are not strictly antisymmetric, contrary to expectations of a pure shift—this lack of strict antisymmetry is also seen in Figure 1g in which the increase in THG to the blue of the resonance center frequency is greater in magnitude than the decrease in THG to the red of the resonance center.[16, 50, 51] The sizes of the positive (red) and negative (blue) lobes are unequal and depend on the pump color, and the dominant lobe differs between SHG (stronger negative) and THG (stronger positive) probes under the same pump excitation (cf. Figures 1h and i). Furthermore, the probe spectrum is strongly non-symmetric about $T = 0$ (see Figure 2d-f) which runs counter to the expectation of Equation 1. These unusual behaviors cannot be explained by the incoherent population contributions because these contributions are negligible for certain pump colors (Figure 2d).

To understand the differences between the conventional optical Stark effect and its manifestation in optical harmonic generation, we employed the well-known perturbative expansion technique to a two-level system.[13, 52] This expansion technique determines the non-linear response through a series of coherent, time-ordered interactions with the pump and probe. Relevant diagrams are shown in Figure 3 along with their $T = 0$ line shapes. Figure 3a shows the optical Stark effect in a transient absorption measurement and its pump-probe frequency response. The perturbative technique representation differs from Figure 1b in that it does not explicitly solve for the hybridized states; it does, however, explicitly treat the probe polarization. Extension of the perturbative method tooOptical harmonic generation is trivial and discussed in the Supplemental Material[45].

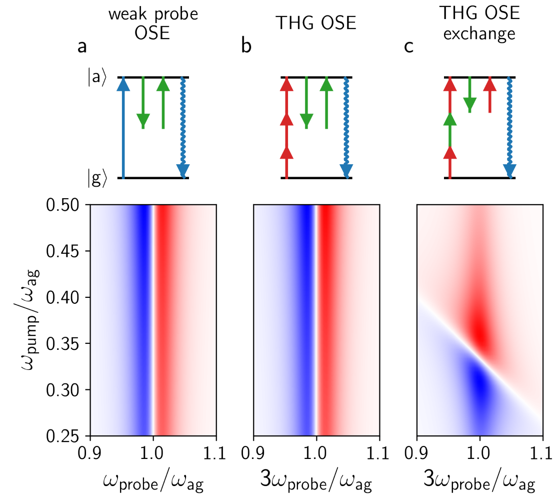

FIG. 3. Representations of the optical Stark effect using wave-mixing energy level (WMEL[53]) diagrams (first row) and their corresponding 2D frequency response (second row) at $T = 0$. Straight arrows represent interactions of the input fields: the resonant weak field probe (blue),the detuned pump (green), and the probe fundamental (red). The wavy blue arrow represents the emission of the signal field. Time flows from left to right. The 2D responses have a dephasing rate of $\Gamma = 0.025\omega_{ag}$ (see the Supplemental Material[45] for details).

The perturbative treatment recovers two processes that alter THG. The first is a direct optical Stark effect analogue for THG (Figure 3b), in which the third harmonic polarization is dressed by the pump and the THG resonance blue shifts. In the second process (Figure 3c), a triple-sum frequency (TSF,[8] $\omega_{\text{TSF}} = 2\omega_{\text{probe}} + \omega_{\text{pump}}$) polarization is dressed by the probe and pump fields. The new process arises because the pump and probe have similar frequencies, so their roles in harmonic generation and dressing the system can exchange. This pathway's 2D spectrum can be understood as a blue-shift of the $\omega_{\text{TSF}} = \omega_{ag}$ TSF resonance, which explains the negatively sloped node. This manifestation of the optical Stark effect is unique to optical harmonic generation because in the weak probe case, degeneracy of the pump and probe frequencies implies the pump is at resonance, where incoherent excitation (carrier populations) or strong field Rabi cycling effects will dominate.

As derived in the Supplemental Material[45] (cf. Equation S79), the net THG Stark effect is a weighted sum of the two Figure 3 THG line shapes. The THG-OSE exchange is weighted three times larger than THG-OSE due to permutation symmetries of the pump and probe fields; for n-th harmonic generation, there is an n-factor weighting. In effect, the optical Stark effect depends strongly on both pump and probe frequencies. When pump and probe frequencies differ greatly (e.g. $\omega_{\text{pump}}/\omega_{ag} \approx 0.5$), the THG-OSE effect is clearly resolved, and a blue shift along the probe axis will result. Near pump-probe degeneracy, however, the exchange pathway is prevalent, and a blue-shift normal to the TSF resonance is seen. Importantly, the blue shift from the exchange pathway enhances THG for $\omega_{\text{pump}} > \omega_{\text{probe}}$ and suppresses THG for $\omega_{\text{pump}} < \omega_{\text{probe}}$. This observation explains the spectral asymmetry of the observed OHG-OSE for both the cases of THG (e.g. Figure 2d) and SHG (e.g. Figure 1h).

Figure 4 compares a simulation of pump-THG-probe with the experiment. The simulation uses a numerical integration technique to account for a small pump-probe delay[54–56] and is similar to a weighted sum of the Figure 3 THG line shapes. When the pump is well above degeneracy ($\hbar\omega_{\text{pump}} \approx 1$), the THG blueshift is clearly resolved. Crucially, when the probe and pump are scanned about degeneracy, the TSF blueshift is clearly seen, an unambiguous confirmation of the THG-OSE exchange process.

Although this simulation shows the importance of the quantum interference between pathways, it only roughly reproduces the asymmetric dynamics about $T = 0$ (compare Figure 2 to Figures S8 and S9 in the Supplemental Material[45]). We believe this difference results because non-perturbative, higher-order effects must be taken into account to fully reproduce the dynamics in Figure 2d-f.[57] Higher order effects are evidenced in our data by the pump induced 2PA and a probe-induced Stark effect (7 meV blueshift, Figure S11 in the Supplemental Material[45]), indicating an eight-wave mixing formalism or higher is required to fully account for the asymmetric dynamics, which is a goal for future work.

Dissipative coupling of the pump, through multiphoton absorption, competes with the coherent optical Stark effect and gives the long-lived "bleach" signals clearly seen at delays longer than pulse overlap, $T > 100$ fs. Multiphoton absorption is interesting for two opposing reasons: for pump-probe applications, it is a useful excitation mechanism because it reduces excitation pulse scatter;[9] for ultrafast modulation applications, it diminishes the time resolution from the optical Stark ef-

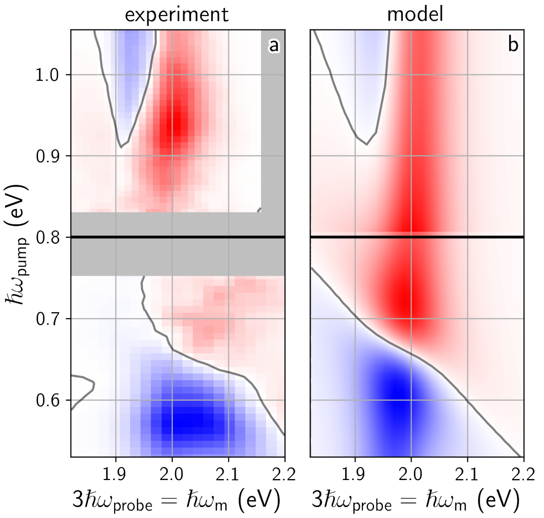

FIG. 4. Comparison between experiment and perturbative expansion model of the optical Stark effect for THG including finite pulse effects ($\hbar\omega_{ag} = 1.98$ eV, $\hbar\Gamma = 36$ meV $\Rightarrow T_2 = 18$ fs, and $\Delta_t = 50$ fs). Experimental data are for $T = -0.01$ ps. The upper and lower halves of (a) and (b) each have their own colormap extent with red (blue) being an increase (decrease) in harmonic generation upon pump excitation. Data in (a) were normalized by the frequency-dependent pump intensity.

fect, so it may be a parameter to minimize. For optimizing ultrafast optical Stark effect modulation, it is beneficial to keep the pump color below the 2PA pump threshold $\hbar\omega_{\mathrm{pump}} < E_0/2$ and close to pump and probe fundamental degeneracy, where the optical Stark effect exchange is enhanced. Our two level model suggests contrast is also increased by using higher-order harmonics; as n increases, the relative contribution of the optical Stark effect exchange process increases (due to the number of pulse permutations), and the degeneracy point $\omega_{\mathrm{pump}} = \omega_{\mathrm{probe}} = \omega_{ag}/n$ occurs at frequencies well below the 2PA onset. This prediction holds when comparing SHG and THG; the SHG-OSE is hard to isolate because the resonance enhancement overlaps with the 2PA onset (see Figure S10 in the Supplemental Material[45]). The OHG-OSE exchange process should also be strong for $n > 3$ and be sensitive to a wide variety of state symmetries through even vs. odd harmonic orders.[3, 7, 58] For high enough harmonics, however, our description will break down because the mechanism of harmonic generation becomes non-perturbative.[59, 60]

To study how the pump fluence affects the optical Stark effect in harmonic generation, we tuned the pump to the 2PA threshold,$\sim$0.99 eV, and measured the change in THG for pump fluences of 500 to 7000 $\frac{\mu\mathrm{J}}{\mathrm{cm}^2}$ (i.e. 1 to 20 $\frac{\mathrm{V}}{\mathrm{nm}}$) At the lowest fluence used, signal is only seen near $T = 0$; the coherent, short-lived optical Stark effect dominates (Figure 5a). As expected for a multi-photon mechanism, however, the prominence of the population signal increases with increased pump fluence. At a sufficiently high fluence to suppress the majority ($\sim$ 70%) of the THG resonance the persistent population signal is almost as large as the peak signals near $T = 0$ (Figure 5b). Figure 5d,e show the fluence scaling trends of the population and optical Stark effect signals. The optical Stark shift scales linearly with pump fluence as expected from Equation 1. The population response (Figure 5e) scales as $\mathcal{F}_{\mathrm{pump}}^{1.4}$, while 2PA is expected to scale as $\mathcal{F}_{\mathrm{pump}}^{2}$, or to saturate at high fluence. The discrepancy in scaling behavior is not understood, although the optical Stark effect is known to introduce surprising fluence scaling due to dynamic resonance conditions and broadening.[19] Our excitation density may also be large enough to modify intra- and inter-exciton forces, which would complicate the fluence scaling.[61, 62]

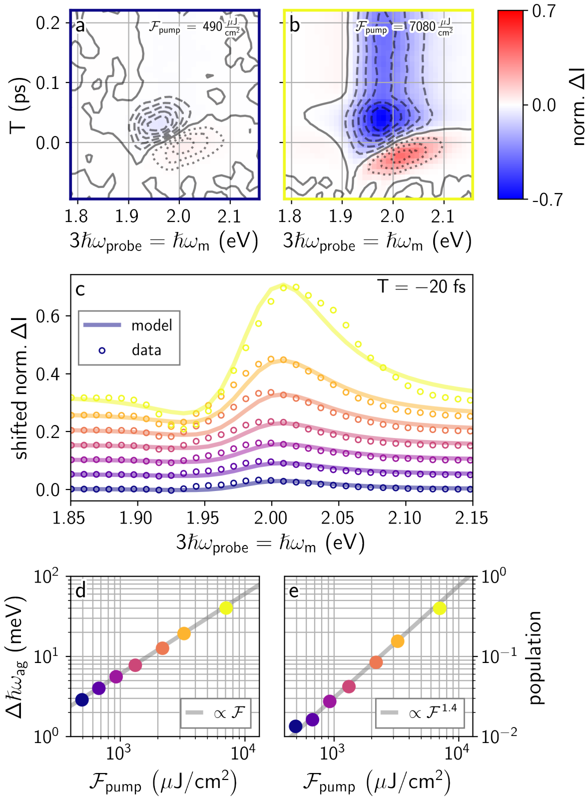

FIG. 5. Effects of pump fluence and pump-probe time delay on WS$_2$ THG spectrum when $\hbar\omega_{\mathrm{pump}} = 0.99$ eV. (a,b) Time delay vs. probe frequency for pump fluences of 490 and 7080 μJ/cm^2 (contour lines are locally normalized). (c) $T = -20$ fs slices (color-keyed circles) at various pump fluences and fits (color-keyed lines) of the THG-OSE and THG-OSE exchange. (d) Fluence dependence of the Stark shift, $\Delta\hbar\omega_{ag} \equiv 1/2\ |\mu\mathcal{E}_{\mathrm{pump}}|^2(\omega_{ag} - \omega_{\mathrm{pump}})^{-1}$ (see Equation S80 in the Supplemental Material[45] for details). (e) Population response (peak norm. ΔI amplitude after 0.1 ps) vs. pump fluence.

We also measured multidimensional pump-THG-probe in a variety of WS$_2$ morphologies to further investigate the balance of absorptive and coherent processes (see Figures S11-S19 in the Supplemental Material[45]). We find that a crystalline monolayer exhibits a sharp 2PA pump color onset at $\hbar\omega_{\text{pump}} = E_0/2$, a narrow THG resonance, and roughly quadratic fluence scaling of the population. However, a polycrystalline thin film exhibits a broad 2PA pump color onset, a broad THG resonance, and roughly linear fluence scaling of the population. Other morphologies examined are in between these behaviors.

In this work we investigated both coherent and incoherent alteration of resonant harmonic generation in WS_2 from an intense, sub-band edge pump. The pump field not only shifts the resonant transition in a manner similar to the traditional optical Stark effect with a single photon probe, but also exchanges with the probe field, resulting in a novel way to modulate harmonic generation. Perturbation theory adequately describes the multidimensional spectral and dynamic characteristics and will be essential for interpreting pump-OHG-probe spectra near the temporal overlap regime. The OHG-OSE exchange mechanisms may also have important applications in ultrafast photonic signal modulation.

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