First Observations of Ultrafast Magneto-electric Charge Separation and Induced Molecular Rotations

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Abstract: We report harmonic generation mediated by magneto-electric charge separation in pentacene and optically-induced magnetization in a series of liquid tetrahalides for the first time.© 2019 OSA
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1. Introduction

The control of magnetic properties of materials by ultrafast optical field enable novel sensing technology, energy conversion, terahertz emission, ultrafast optical switching, and ultrafast data storage. However, the interaction of the magnetic field of light with materials is normally ignored due to low magnetic susceptibilities at high frequencies. Magnetic response of materials with light can be enhanced by nanoscale engineering of materials such as metamaterials[1]. Very recently, it has been reported that magnetic properties of homogeneous dielectric media can be controlled by optical nonlinearities driven jointly by electric and magnetic field components of light [2-4]. In this paper, we present two novel phenomena arises from magneto-electric (ME) nonlinearities: (i) optically induced magnetization which is originated from magnetic torque induced molecular rotation in a series of tetrahedral molecules, and (ii) charge separation in pentacene thin film induced by the coupling of magnetic and electric fields of light.

2. Optically induced magnetization

The enhancement of magnetic response at molecular level by light has been described by a quantum theory wherein the magnetic field of light exerts a torque on orbital angular momenta and induces molecular libration [3]. However, no spectral observations have yet been reported. Here, we present observations of Stokes-shifted librations and vibrations obtained by measuring linearly-polarized magnetic dipole scattering using a femtosecond laser. The observations provide direct evidence that strongly supports the quantum theory of torque-mediated optical magnetization.

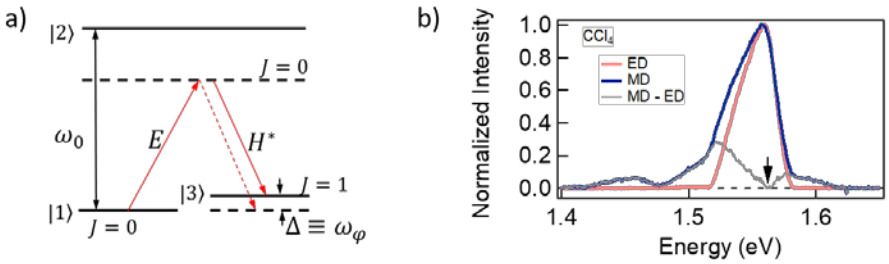

Figure 1. (a) Two-level diatomic molecule diagram of magneto-electric scattering model involves E and B* fields. (b) Normalized magnetic-, and electric-dipole (ED, MD) spectra of scattered light in CCl_4, the grey curve is the difference of MD and ED.

Figure 1 (a) depicts a two-level diatomic molecule diagram of the scattering mechanism in which magneto-electric optical process induces strong magnetization. A dual optical field, E and H*, drives the interaction. The first photon excites the molecule from an L=0 ground state to a virtual excited state with orbital angular momentum L=1; the second photon exerts a magnetic torque to generate a molecular libration/rotation. This model predicts a Stokes-shifted Raman interaction at sideband frequency $\omega-\omega_\phi$, where ω and ω_ϕ are optical and molecular rotational frequencies, respectively. The induced molecular rotations/librations results in a large magnetic moment. Figure1 (b) shows the co-polarized (ED, red) and cross-polarized (MD, blue) scattering spectra of CCl_4 plot along with the incident laser spectrum (black). The ED spectrum consists of Rayleigh-scattered light which is similar to the laser spectrum. Intriguingly, the MD spectrum clearly shows broadening to the red by an amount ~12 meV together with Stokes (at 1.46 and 1.503 eV) and anti-Stokes (at 1.596 eV) Raman peaks. The 12 meV red-shift for the MD

spectrum is close to the rotational energy of 14 meV for CCl_4. Similar results were obtained for other tetrahedral molecules. The results indicate that the dual interaction of magnetic and electronic field results in a molecular rotation that enhanced the magnetic dipole moment.

3. Magneto-electric charge separation

The strong coupling between electric and magnetic fields of light drives the bound electrons to move in an arc curve, Fig 2a [2]. Such the curved motion of charge breaks the system symmetry. As a result, it raises several unforeseen physical phenomena such as longitudinally polarized second harmonic radiation, induced transverse magnetization at the optical frequency, and charge separation along the propagation direction. Here we focus on the study of ME charge separation. We chose pentacene organic semiconductor as a model material for this investigation. The pentacene thin film was prepared by thermal deposition on a glass substrate in a high vacuum. The sample was then kept in an inert gas environment during both storage and measurement to avoid photo-oxidation. We utilized time-resolved second harmonic generation technique to investigate an ME charge separation. A femtosecond laser beam acted as an optical pump to induce ME charge separation. The DC electric field from the ME charge separation interacted with the optical field from a second laser beam, the probe, in a four-wave-mixing interaction that induced second harmonic (M-EFISH) generation. By monitoring time-resolved M-EFISH, we were able to study the ME charge separation dynamics.

Figure 2b shows the pump-induced EFISH signal as a function of pump-probe delay. The pump and probe photon energies were set at 1.55 eV, well below the bandgap of pentacene. At zero delay, the EFISH signal reaches the highest value and rapidly decay with a time constant of 0.5 ps. The charge separation is generated by electric and magnetic components of light acting together in a nonlinear two-photon process. The quadratic power dependence of the pump-induced SHG change in Fig. 2c indicates that the change of the EFISH signal (amount charge separation) is indeed a second order process.

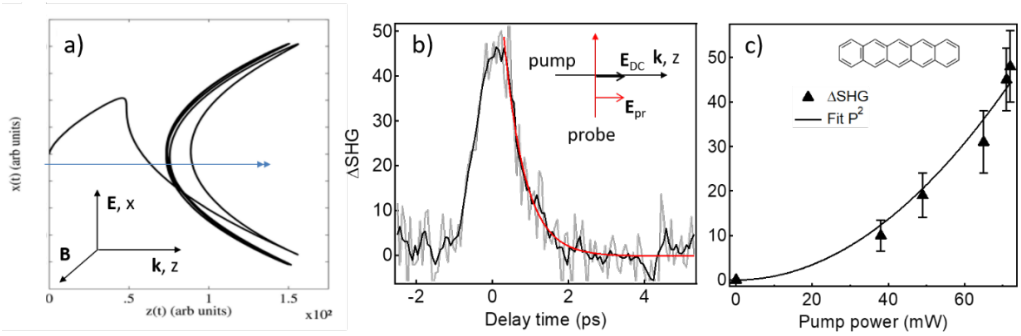

Figure 2. (a) Calculated trajectory of electron motion subject to the Lorentz force at an incident electric field strength of 10^8 V/m [2]. (b) Pump-induced EFISH signal from the pentacene thin film using a pump-probe setup. Inset: Pump-probe cross beam geometry. (c) Quadratic pump power dependence of pump-induced SHG. Inset: pentacene molecule structure.

Conclusions

We have observed Stokes-shifted librations/rotations and vibrations exclusively in magnetic dipole scattering spectra of tetrahedral molecules including CCl_4. The observation of stimulated librations in magnetic scattering is direct evidence strongly supporting the recent quantum theory of magneto-electric interactions [3]. In particular, the experiments provide direct evidence of torque-mediated enhancement of optical magnetization. In the second part, we used an electric field induced second harmonic generation technique to demonstrate for the first time the charge separation in a pentacene thin film at nonrelativistic intensities by magneto-electric nonlinearity.

Acknowledgments

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