Magnetic Dipole Scattering from 3D-conjugated LUMOs in Silsesquioxanes

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Abstract: Cross-polarized light scattering in silsesquioxane (SSQ) molecules probes the azimuthal variation of intramolecular potentials. SSQ molecules with small and large cage interiors reveal variations in the sphericity of orbital shapes for the first time.
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1. Introduction

At optical frequencies, magnetic dipole transitions are usually neglected due to their weak nature compared to strong electric dipole counterparts. Interestingly in recent years it has been shown that, at intensities as low as 10^9 W/cm^2 (far below relativistic intensities), the magnetic field can induce response on a par with electric dipole interactions. In cross-polarized light scattering in solids and liquids [1,2], magneto-electric (M-E) nonlinearities have been reported that induce magnetization at optical frequencies in isotropic molecules. Quantum theoretical analysis of induced magnetic scattering has revealed that the intensity and polarization properties of magnetically scattered light are governed primarily by the natural frequency of libration ω_ϕ of excited electrons. This motion depends on the azimuthal slope of the intra-molecular potential V according to $\omega_\phi = [(1/I)\mathrm{d}V/\mathrm{d}\phi]^{1/2}$, where I is the moment of inertia [3,4]. In this paper we show that nonlinear scattering experiments can distinguish between subtle shape differences in the 3D-conjugated LUMO at the center of silsesquioxane cage structures in an unique way that exploits their susceptibility to 2-photon, magneto-electric transitions.

2. Experimental Results and Discussion

Figure 1 (a) is a two-level diagram depicting the 2-photon (magneto-electric) scattering mechanism that induces strong magnetic scattering [3]. Two optical fields, E and B, initiate the interaction. A first photon excites the molecule from the ground L=0 state to a virtual excited state with orbital angular momentum L=1; a second photon exerts magnetic torque that converts orbital to rotational (librational) angular momentum. In the second step, the

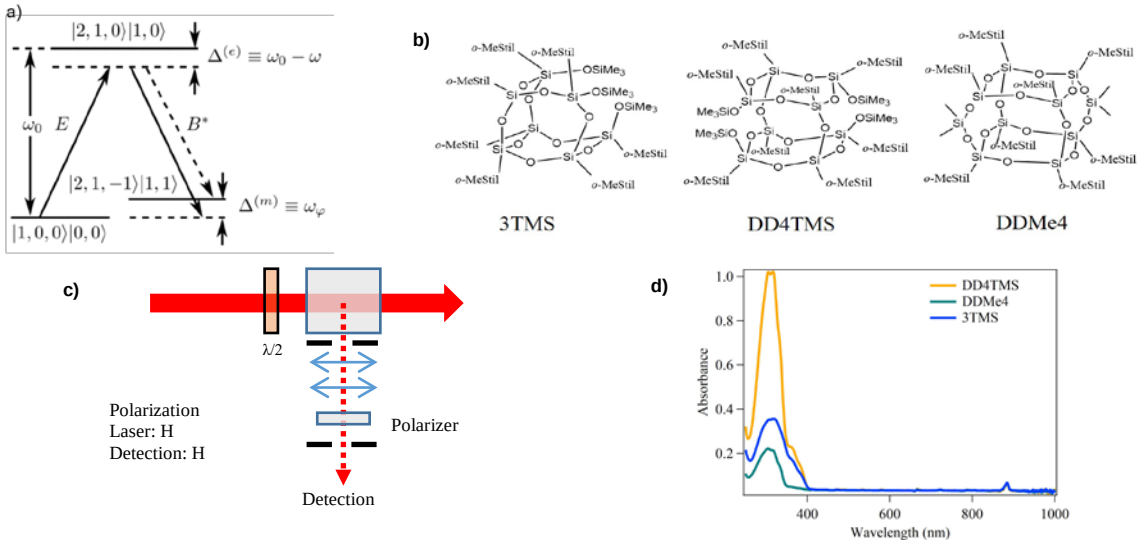

Figure 1. (a) Two-level diagram of magneto-electric scattering model, (b) Molecular Structures (c) Setup for scattering experiment; H represents horizontal polarization (d) Absorption Spectra of the studied compounds in dichloromethane solvent

orbital magnetic moment is enhanced while the molecule undergoes electronic de-excitation. Figure 1(b) represents the molecular structure of three samples that were studied and Figure 1(c) is a schematic of the experimental setup.

The experiment utilized an amplified femtosecond Ti:sapphire laser system operating at 10 kHz with tunable bandwidth and pulse durations from 20 to 100 fs at a central wavelength of 800 nm. The experimental setup (Fig. 1c) included a motorized rotating half-wave plate in the incident beam to control the incident light polarization. A polarizer in the detection path was used to select polarization of light transmitted to the detector. The scattered photons were detected at 90° with respect to the incident beam using a photomultiplier tube. A pair of convex lenses with focal lengths of 150 cm were placed in the detection path to collect scattered light. An iris determined the collection solid angle, deliberately kept small to avoid off-axis electric dipole (ED) signals from contributing to the magnetic dipole (MD) radiation pattern. The silsesquioxanes samples were prepared in dichloromethane solvent and were studied in 1x1 cm^2 quartz cuvettes. The molecules studied were o-$MeStil_7T_7(TMS)_3$ abbreviated as 3TMS, o-$MeStil_8DD(TMS)_4$ abbreviated as DD4TMS and o-$MeStil_8DDMe_4$ abbreviated as DDMe4. The molecular structures are shown in Fig. 1(b) and their absorption in 1 (d) respectively.

Figure 2 shows the co-polarized (ED, red) and cross-polarized (MD, blue) radiation patterns of the respective compounds. Two separate components are visible in the scattering data, one with a (polarized) purely dipolar variation and another which contributes a constant background (unpolarized). Both components are of magnetic origin. The relative magnitudes of these two components varies with the magnitude of the natural frequency of libration of the active electrons and may be interpreted with the help of Fig. 1a and quantum theory [4]. On an experimental basis we noted that the polarized MD component is only present in TMS, while absent in DD-4TMS and $DDMe_4$. There is no angular variation of the MD signal in DD4TMS or DDMe4. The TMS molecule has corner capped edges whereas the other molecules have intact corners. The proportion of unpolarized to polarized MD components is heightened by decreasing librational frequency ω_ϕ. Presuming the active electron density occupies the orbital centered in the cage, the trend is consistent with resonance frequencies in the order

$$\omega_\phi(\text{TMS}) > \omega_\phi(\text{DD-4TMS}) \approx \omega_\phi(\text{DDMe}_4)$$

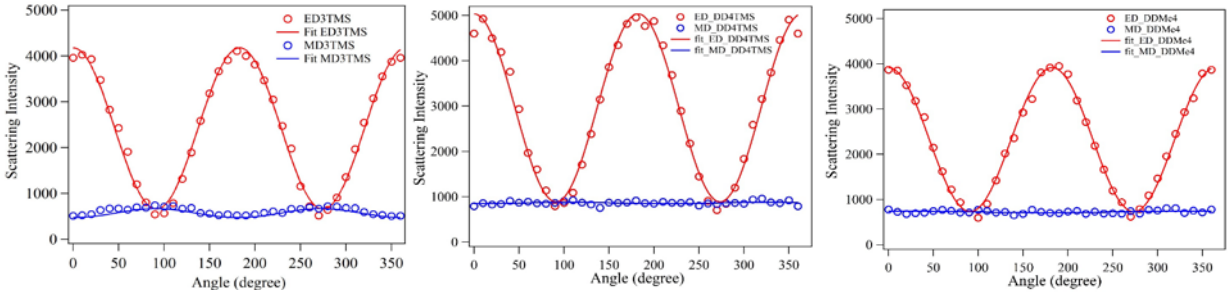

Figure 2. Radiation patterns of scattering by induced electric and magnetic dipole moments in the medium. The data were measured through an analyzer which either selects Rayleigh scattering (red) or blocks it (blue). These data sets reveal the relative magnitudes of electric dipole and magnetic dipole moments induced in the sample by incident light at 800 nm at fixed power.

3. Conclusions

In the quantum model of magneto-electric coupling, it is the slope of the orbital potential function that regulates the torsional restoring force. A nearly spherical potential has a slope close to zero which promotes unpolarized MD scattering (because the rotation-generating channel becomes resonant with the light frequency). The scattering data are therefore consistent with the idea that altering the molecular skeleton in the TMS compound distorts the sphericity of the electron orbital in the cage. It is quite reasonable to expect that the electron potential develops an axis passing through the corner from the center of the cage due to the open corner of the TMS structure. The introduction of this axis may be argued to increase the ED transition moment and the anisotropy of the potential thereby raising the librational frequency and diminishing the magnetic scattering intensity. Thus the scattering experiments suggest there is a modest reduction in the sphericity of the LUMO in the cage when a corner is opened.

4. References

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