Chiral Light-Matter Interaction in Optical Resonators

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The Purcell effect explains the modification of the spontaneous decay rate of quantum emitters in a resonant cavity. For quantum emitters such as chiral molecules, however, the cavity modification of the spontaneous decay rate has been little known. Here we extend Purcell's work to the chiral light-matter interaction in optical resonators and find the differential spontaneous decay rate of chiral molecules coupled to left and right circularly polarized resonator modes. We determine the chiral Purcell factor, which characterizes the ability of optical resonators to enhance chiroptical signals, by the quality factor and the chiral mode volume of a resonator, representing, respectively, the temporal confinement of light and the spatial confinement of the helicity of light. We show that the chiral Purcell effect can be applied to chiroptical spectroscopy. Specifically, we propose a realistic scheme to achieve resonator enhanced chiroptical spectroscopy that uses the double fishnet structure as a nanoscale cuvette supporting the chiral Purcell effect.

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Molecules that cannot be superimposed on their mirror images, known as chiral molecules, interact differently with circularly polarized light depending on the handedness of polarization. Chiroptical spectroscopy exploits left and right circularly polarized plane waves to obtain stereochemical information for chiral molecules. Chiroptical signals, however, are inherently weak because the length of chiral molecules is much smaller than the wavelength of light. Recently, it has been suggested that the problem of weak chiroptical signals can be overcome by utilizing locally varying electromagnetic fields instead of circularly polarized plane waves [1–3]. Subsequently, significant effort has been made to find various nanostructures that excite localized electromagnetic fields and enhance chiroptical signals, such as plasmonic nanostructures [4–7], nanoantennas [8], dielectric nanoparticles [9], and negative-index metamaterials [10]. However, little is known about the mechanism behind the ability of nanostructures to modify the differential spontaneous decay of chiral molecules that are coupled to two opposite circularly polarized modes in terms of the local density of states. In contrast, the Purcell effect successfully explains the enhancement by optical resonators of the spontaneous decay rate of achiral molecules. The Purcell factor F_P, the figure of merit for the cavity enhancement of the spontaneous decay rate, is determined solely by the cavity parameters quality factor (Q) and mode volume (V) [11,12], such that $F_P = (3/4\pi^2)(\lambda_0/n)^3(Q/V)$, where (λ_0/n) is the effective resonance wavelength within a medium of refractive index n.

In this Letter, we extend Purcell's work to the chiral light-matter interaction in optical resonators. We obtain a figure of merit, the chiral Purcell factor F_C, for the cavity-modified spontaneous decay rate of chiral molecules that is comparable to the Purcell factor F_P. The chiral Purcell factor F_C is determined by the cavity parameters quality factor (Q) and chiral mode volume (V_C). The newly defined V_C is given by the ratio between the total energy of the resonator U and the maximum local optical chirality C, which is a measure of the local helicity of light [1,13,14]. Thus, the chiral mode volume V_C represents the spatial confinement of light helicity, while the quality factor Q represents the temporal confinement of light. We also discuss the feasibility of resonator enhanced chiroptical spectroscopy utilizing the chiral Purcell effect. Specifically, we choose a resonator structure formed by cavities of double fishnet metamaterials that also act as a nanoscale cuvette containing chiral molecule samples. We show that the proposed double fishnet cavity structure, easily fabricable via nanofabrication techniques, possesses the chiral Purcell factor $F_C = 138$. This results in a strong enhancement of circular dichroism (CD) and fluorescence detected circular dichroism (FDCD), representing the differential absorption and emission of left and right polarized light, respectively. When averaged over the entire cavity region, the (FD)CD enhancement factor becomes the order of tens, thereby showing good promise for resonator enhanced chiroptical spectroscopy to detect small quantities of chiral molecules.

A chiral molecule possesses an electric dipole moment $\mathbf{p} = p\mathbf{u}$ and a magnetic dipole moment $\mathbf{m} = m\mathbf{v}$, where $\mathbf{u}$ and $\mathbf{v}$ are real unit direction vectors and magnitudes p and m are pure real and pure imaginary, respectively [15,16]. The spontaneous decay rate of a chiral molecule is given by $\Gamma = 2\mathrm{Im}[\mathbf{p}^* \cdot \mathbf{E}(\mathbf{r}_0) + \mathbf{m}^* \cdot \mathbf{B}(\mathbf{r}_0)]/\hbar$ [17,18], where $\mathbf{E}(\mathbf{r}_0)$ and $\mathbf{B}(\mathbf{r}_0)$ are the electric and magnetic fields, respectively, at $\mathbf{r} = \mathbf{r}_0$ in the cavity. To calculate the spontaneous decay rate in terms of the cavity parameters, we expand the electromagnetic fields to $\mathbf{E}(\mathbf{r}, \omega) = \sum_{m=1} a_m(\omega)\tilde{\mathbf{E}}_m(\mathbf{r})$

and $\mathbf{B}(\mathbf{r},\omega) = \sum_{m=1} a_m(\omega)\tilde{\mathbf{B}}_m(\mathbf{r})$ using the quasinormal modes $\tilde{\mathbf{E}}_m(\mathbf{r})$ and $\tilde{\mathbf{B}}_m(\mathbf{r})$ of the cavity. The expansion coefficients $a_m(\omega)$ can be determined using the Lorentz reciprocity technique [19,20]. Note that the quasinormal modes correspond to the damped oscillations of the cavity leakage after withdrawing an initial pump beam [21]. Using the decay rate Γ, we can derive the differential decay rate of chiral molecules $\Delta\Gamma(\mathbf{r}_0) = \Gamma^+(\mathbf{r}_0) - \Gamma^-(\mathbf{r}_0)$ coupled to the left $(+)$ and right $(-)$ circular polarization modes of the cavity (see Supplemental Material [25] for a full derivation). Normalizing the differential decay rate $\Delta\Gamma(\mathbf{r}_0)$ in the cavity with the differential decay rate in free space $\Delta\Gamma_0 = -4\omega^3 n \mathrm{Im}[pm]/3\pi\varepsilon_0\hbar c^4$ [15], the differential decay rate modified by a single resonance of the cavity is written as

$$\frac{\Delta\Gamma(\mathbf{r}_0)}{\Delta\Gamma_0} = F_C \frac{\omega_0{}^2}{\omega^2} \frac{\omega_0{}^2}{\omega_0{}^2 + 4Q^2(\omega-\omega_0)^2} \frac{C(\mathbf{r}_0)}{C_{\max}} \eta_C, \tag{1}$$

where F_C, ω_0, and Q are the chiral Purcell factor, the resonant frequency, and the quality factor of the cavity, respectively. The optical chirality $C(\mathbf{r}_0) \equiv -n^2\varepsilon_0\omega \mathrm{Im}[\tilde{\mathbf{E}}^*(\mathbf{r}_0)\cdot\tilde{\mathbf{B}}(\mathbf{r}_0)]/2$ is a measure of how strongly local electromagnetic fields interact with randomly oriented chiral molecules [1], and $C_{\max}$ is the maximal optical chirality inside the cavity. We also define the extended optical chirality as

$$C(\mathbf{r}_0;\mathbf{u},\mathbf{v}) \equiv -\frac{3n^2\varepsilon_0\omega}{2}\mathrm{Im}\{[\mathbf{u}\cdot\tilde{\mathbf{E}}^*(\mathbf{r}_0)][\mathbf{v}\cdot\tilde{\mathbf{B}}(\mathbf{r}_0)]\}. \tag{2}$$

Note that the extended optical chirality $C(\mathbf{r}_0;\mathbf{u},\mathbf{v})$ can be reduced to optical chirality $C(\mathbf{r}_0)$ using the rotational average $\langle C(\mathbf{r}_0;\mathbf{u},\mathbf{v})\rangle_{\mathrm{rot}} = C(\mathbf{r}_0)$. The orientation factor $\eta_C = C(\mathbf{r}_0;\mathbf{u},\mathbf{v})/C(\mathbf{r}_0)$ represents orientation matching between dipole moments and electromagnetic fields.

The chiral Purcell factor F_C is defined as

$$F_C \equiv \frac{1}{4\pi^2}\left(\frac{\lambda_0}{n}\right)^3\left(\frac{Q}{V_C}\right). \tag{3}$$

The chiral mode volume V_C is defined as

$$V_C \equiv -\frac{\omega U}{cC_{\max}} = \frac{U}{u_{C,\max}}, \tag{4}$$

where U and $u_{C,\max}$ are the total energy of the cavity and the maximum chiral energy density inside the cavity, respectively. They are given explicitly by $U = (1/4)\int\{[\partial(\omega\varepsilon)/\partial\omega]|\tilde{\mathbf{E}}|^2 + [\partial(\omega\mu)/\partial\omega]|\tilde{\mathbf{H}}|^2\}d^3\mathbf{r}$ and $u_{C,\max} = -cC_{\max}/\omega$, where ε and μ are permittivity and permeability, respectively. It is noteworthy that the chiral energy density u_C is related to the helicity of light $K = -u_C/\omega$, which is the degree of circular polarization in the plane wave representation [14]. Although helicity has only been defined for plane waves [13,14], we can hypothesize that $K(\mathbf{r}_0)$ refers to the local helicity of the electromagnetic near fields in optical resonators. Consequently, the chiral mode volume can be interpreted as the confinement of local helicity with respect to space. The chiral mode volume V_C may be compared to the mode volume $V = U/2u_{E,\max}$ with the energy density of electric fields $u_{E,\max} = \varepsilon_0 n^2|\tilde{\mathbf{E}}_{\max}|^2/4$.

Importantly, the modification of the differential spontaneous decay rate $\Delta\Gamma/\Delta\Gamma_0$ by optical resonators can be utilized for the enhancement of circular dichroism (CD) and fluorescence detected circular dichroism (FDCD) signals of a chiral molecule. CD spectroscopy measures difference in the absorption of left versus right circularly polarized lights by a chiral molecule, while FDCD spectroscopy measures the difference in fluorescence intensity for left and right circularly polarized excitations [22,23]. In CD spectroscopy, the normalized differential absorption $\Delta A/\Delta A_0$ is equivalent to the normalized differential decay rate $\Delta\Gamma/\Delta\Gamma_0$ as they are related by the Beer-Lambert law, $\Delta A = (\Delta\varepsilon)lc = (\hbar\omega N_A \Delta\Gamma/4)lc$ with differential molar absorptivity $\Delta\varepsilon$, Avogadro number N_A, path length l, and molecular concentration c [15,24]. In FDCD spectroscopy, the normalized differential decay rate $\Delta\Gamma/\Delta\Gamma_0$ accounts for the enhancement of differential fluorescence of a molecule when the fluorescence efficiency is high [22,23]. Henceforth, $\Delta\Gamma/\Delta\Gamma_0$ will be referred to as the (FD)CD enhancement.

To demonstrate the feasibility of the high chiral Purcell factor, we analyze an exemplary Fabry-Perot cavity resonator (see Supplemental Material [25] for the calculation of the quasinormal modes of the Fabry-Perot cavity). The Fabry-Perot resonator modes are confined along the z direction with cavity length $L_z = d$. We assume a diffraction-limited lateral cavity width $L_x = L_y = \lambda_0/2$ [35], where λ_0 is the lowest order resonance wavelength. The chiral mode volume is given by $V_C = (\lambda_0/2)^2\int\{[\partial(\omega\varepsilon)/\partial\omega]|\tilde{\mathbf{E}}|^2 + [\partial(\omega\mu)/\partial\omega]|\tilde{\mathbf{H}}|^2\}dz/4u_{C,\max}$. We also assume that cavity mirrors preserve polarization upon reflection [36,37] to build up high chiral energy density u_C inside the cavity. With typical values for cavity parameters and randomly oriented chiral molecules, explicit calculation in Fig. 1 shows that the (FD)CD enhancement $\Delta\Gamma/\Delta\Gamma_0$ indeed reached up to 10^2, thereby suggesting the possibility of resonator enhanced chiroptical spectroscopy. We also find that the dissymmetry factor $g \equiv \Delta\Gamma/\bar{\Gamma} = 2(\Gamma^+ - \Gamma^-)/(\Gamma^+ + \Gamma^-)$, which is a measure of chiroptical signal sensitivity, can be simultaneously enhanced. The volume-averaged dissymmetry factor can be enhanced up to 10^3 inside the Fabry-Perot resonator (see Supplemental Material [25]).

For a more realistic application to chiroptical spectroscopy, we propose a prototype metamaterial resonator consisting of a double fishnet structure as shown in

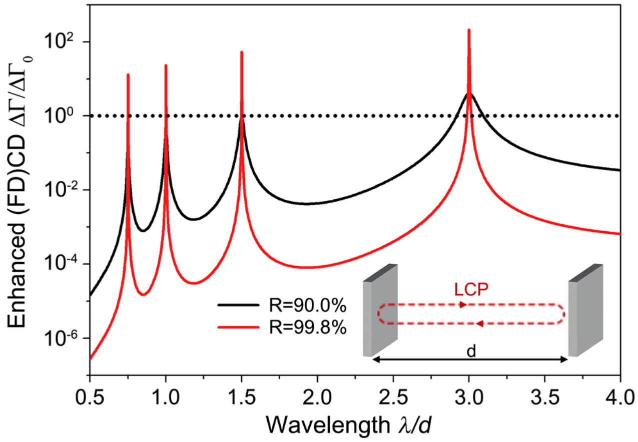

FIG. 1 (color online). Enhanced (FD)CD $\Delta\Gamma/\Delta\Gamma_0$ of a polarization-preserving cavity with mirror reflectivity $R = 90.0\%$ (black line) and 99.8% (red line) and a chiral molecule sample with refractive index 1.5. Inset shows the polarization inside the two cavities.

Fig. 2. The double fishnet structure comprises a dielectric layer (35 nm hydrogen silsesquioxane) sandwiched between two metal layers (30 nm silver) on a glass substrate. In order to contain chiral molecules such as flavin mononucleotide exhibiting chiroptical signals in the visible spectral range, the metal-dielectric-metal (MDM) layer is perforated by square cavities (sides $a = 200$ nm and lattice constant $h = 320$ nm). While the double fishnet structure metamaterial has been originally suggested for realizing the negative index of refraction, recently it has been reported that double fishnet structures can uniformly enhance optical chirality inside square cavities [10]. Thus we may possibly use metamaterial cavities as a nanoscale cuvette supporting the chiral Purcell effect, and measure the enhanced (FD)CD signals of chiral molecules.

In order to confirm the potential of metamaterial resonator, we calculate the chiral Purcell factor of the double fishnet structure numerically using the finite-difference time-domain (FDTD) method. In numerical calculation, we use the refractive indices of silver and HSQ from measured data [38,39] and excite resonant modes of the double fishnet structure by an initial short input pulse [36,37]. The chiral mode volume and the quality factor are extracted from FDTD results using the filter diagonalization technique [40]. From these results, we find that significant enhancement of (FD)CD $\Delta\Gamma(\mathbf{r})/\Delta\Gamma_0$ occurs inside the square-shaped metamaterial cavity at resonance wavelengths $\lambda_{0,1} = 897$ nm and $\lambda_{0,2} = 677$ nm as shown in Fig. 3(a). The mode at $\lambda_{0,1} = 897$ nm possesses the chiral Purcell factor $F_C = 132$, the quality factor $Q = 193$ and the chiral mode volume $V_C = 3.70\lambda_{0,1}{}^3 \times 10^{-2}$. Another mode at $\lambda_{0,2} = 677$ nm possesses the chiral Purcell factor $F_C = 3.08$, the quality factor $Q = 12.5$ and the chiral mode volume $V_C = 1.03\lambda_{0,2}{}^3 \times 10^{-1}$. Figure 3(a) shows that enhancement $\Delta\Gamma(\mathbf{r})/\Delta\Gamma_0$ varies

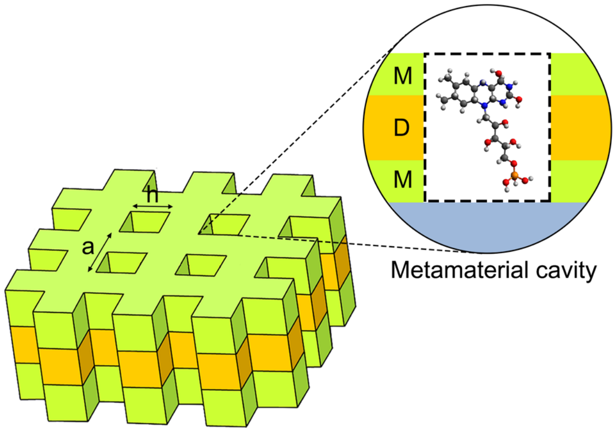

FIG. 2 (color online). Proposed experiment for the chiral Purcell effect using the double fishnet structure. The double fishnet structure comprises metal-dielectric-metal (MDM) multilayers with square-shaped metamaterial cavities of sides h and lattice constant a. Inset shows a vertical cross section of the metamaterial cavity containing flavin mononucleotide, a biomolecule which exhibits chiroptical signals in the visible spectral range.

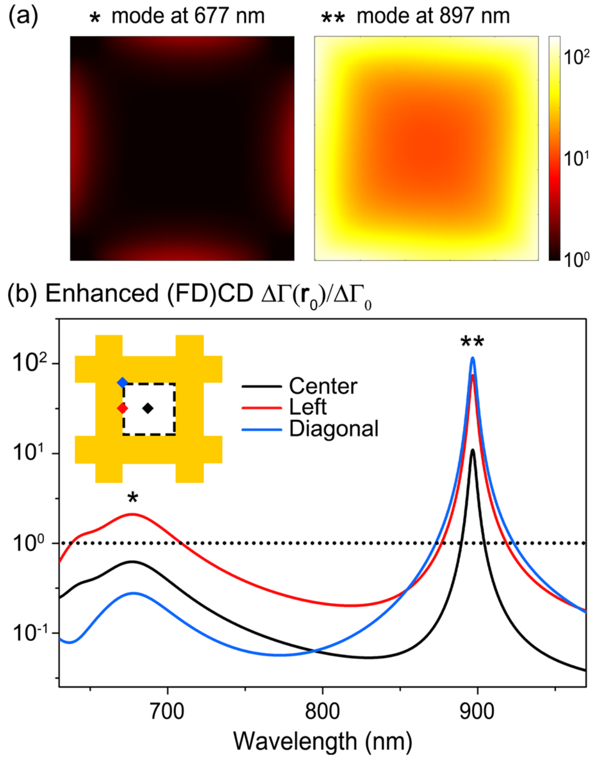

FIG. 3 (color online). (a) Spatial dependence of the local (FD) CD enhancement $\Delta\Gamma(\mathbf{r})/\Delta\Gamma_0$ inside the metamaterial cavity at $\lambda_{0,2} = 677$ and $\lambda_{0,1} = 897$ nm. (b) The (FD)CD spectrum of molecules at the center (black), left (red), and upper left (blue) positions inside the cavity. Inset shows a horizontal cross section of the double fishnet structure and molecular positions (black, red, and blue diamonds).

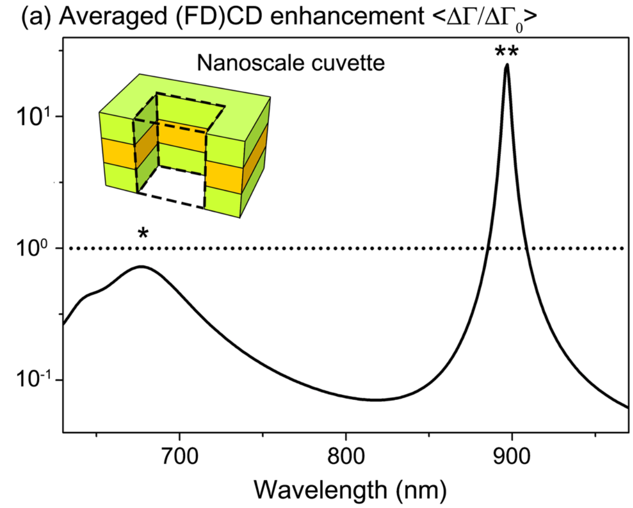

FIG. 4 (color online). Volume-averaged (FD)CD enhancement $\langle \Delta\Gamma/\Delta\Gamma_0 \rangle$ of the double fishnet structure. Inset displays a vertical cross section of the metamaterial cavity region suggested for the nanoscale container of chiral molecules.

locally inside the cavity without changing sign. The spectral behavior of $\Delta\Gamma(\mathbf{r})/\Delta\Gamma_0$ at three distinct locations, given in Fig. 3(b), shows that (FD)CD enhancement can reach to 10^2 at $\lambda_{0,1} = 897$ nm. Strong and uniform enhancement of $\Delta\Gamma(\mathbf{r})/\Delta\Gamma_0$ for the mode at $\lambda_{0,1} = 897$ nm can resolve the difficulty of positioning chiral molecules inside the cavities. Figure 4 shows that, even after the volume averaging, the overall (FD)CD enhancement of the resonant mode at $\lambda_{0,1} = 897$ nm is more than tenfold. Corresponding to molecular species, the resonance wavelength $\lambda_{0,1} = 897$ nm can be spectrally tuned by stacking more MDM layers or controlling the size and lattice constant of the cavities [10,39,41].

For decades, the Purcell effect has offered a wide range of applications such as the surface-enhanced Raman spectroscopy [35], a single-photon source [42], and a nanolaser [43]. Likewise, the chiral Purcell effect we propose in this Letter may open up novel possibilities of the chiroptical spectroscopy, polarization-modulated single-photon sources and nanolasers. On the other hand, Bliokh, Kivshar, and, Nori recently reported that the enhancement of magnetoelectric effects can be achieved in local light-matter interactions in the same manner as chiral light-matter interactions [44]. Similar to chiral molecules, magnetoelectric molecules have a purely real electric dipole moment $\mathbf{p}$ and a purely real magnetic dipole moment $\mathbf{m}$. Thus, the approach taken for the chiral Purcell factor may also hold for the magnetoelectric effect, with the chiral energy density u_C being replaced with the magnetoelectric energy density $u_{\mathrm{me}} \equiv (n^2/2c)\mathrm{Re}[\tilde{\mathbf{E}}^*(\mathbf{r}_0) \cdot \tilde{\mathbf{H}}(\mathbf{r}_0)]$.

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