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Resonant optical trapping and manipulation of nano-objects based on nonlinear optical response

Tetsuhiro Kudo

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Doctoral Thesis at Osaka Prefecture University
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Tetsuhiro Kudo
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Chapter 1

Introduction

1.1 Radiation force

Light has momentum despite the fact that it has no mass, and thus, this momentum causes a force that can move objects. It is well-known that, in space, this phenomenon contributes to form a comet tail pointing away from the sun. This force is called radiation force (radiation pressure), which was predicted by I. Newton and derived theoretically by J. C. Maxwell [1]. P. N. Levedev first experimentally confirmed the existence of the radiation force in 1900 [2], and further, E. F. Nichols and G. F. Hull measured its magnitude in 1901 [3]. In everyday life the radiation force seems to have no influence on an object’s motion because it is too weak to overcome friction or gravity. Therefore, manipulating objects by the radiation force had been quite difficult until the invention of the laser. In 1970, A. Ashkin first experimentally succeeded in manipulating microparticles diffused in a solvent by using a laser [4]. In particular, he demonstrated the transportation of these particles by using a single laser and also managed to trap them by using counter-propagating laser beams. Further, in 1986, A. Ashkin et al. successfully demonstrated the trapping of a single microparticle by using only a single tightly focused laser beam [5].

The radiation force is classified into the dissipative force and the gradient force. The former is induced through dissipation processes such as absorption and scattering, wherein the kinetic momentum of photons is transferred to the particles. On the other hand, the latter arises due to the electromagnetic interaction between the light and the induced polarization. When a focused laser beam irradiates particles, they are trapped at the laser’s focal spot if the gradient force exceeds the dissipative one that pushes particles out of the focal spot. The technique to trap particles based on the latter mechanism is well-known as optical tweezeing, and it has been used in various research fields including biochemistry, materials engineering, and so on [6–20]. For example, the direct observation of the stepping of kinesin (a biological motor) by using optical tweezers with a high spatial
and temporal sensitivity has given impetus to a broad area of research [6].

With the recent development of nanoscience and associated technologies, the size of the trapping targets has been shifting to the nanometer scale. Several experimental demonstrations have been carried out concerning the trapping and manipulation of nanoscale objects such as single organic molecules, their aggregates, metal nanoparticles, quantum dots, and so on [10, 12, 21–30]. Although these demonstrations have indicated interesting possibilities, the optical manipulation of nanoparticles is still challenging because the radiation force decreases in proportion to the particle size, thereby resulting in the quite weak radiation force in nanosized regimes to overcome an environmental disturbance such as that by Brownian motion. To obtain a sufficiently strong radiation force, some approaches have considered using metal nanostructures to obtain localized intense electric fields and steep field gradients [31–37], and using the instantaneous peak intensity of a femtosecond pulsed laser [37–43], etc. Another approach is to utilize the electronically resonant response of the particles. In the electronic resonance condition, the induced polarization is resonantly enhanced, and so is the induced force. Of course, this effect can be combined with those of the localized and instantaneous intense fields.

### 1.2 Resonant optical manipulation

The idea of using an object’s resonance condition for its optical manipulation was first proposed by A. Ashkin [4], and he referred to the possibility of applying this idea to selective accelerating, trapping, or separating the atoms or molecules of gases by using lasers tuned to specific resonances for obtaining the large effective cross sections. It is well-known that this scheme has been used for the laser cooling of atoms [44–48]. For matter systems with considerably greater degrees of freedom, some demonstrations of optical trapping by using the absorption band of organic molecules have been reported [21, 22], wherein favorable results were obtained, and these were attributed to the resonance absorption of molecules. Further, a theoretical demonstration of optical trapping by using a single beam was made for the resonance condition [49]. Although such an induced force for single molecules is very weak, the use of resonance conditions provides some advantages. However, as we explain later, the mechanism underlying the advantages was not clear.

At this time, our group has proposed optical manipulation by using the electronically resonant optical response of semiconductor nanoparticles [50–52], and we have shown that the resonant optical response enables the realization of not only an enhancement of induced force but also a manipulation to sort particles via particular quantum mechanical properties. For example, the possibility of size selective manipulation has been discussed [50]. The resonance frequencies of semiconductor nanoparticles are shifted sensitively to their size in the nanoscale regime. If we tune the incident photon frequency to the
resonance level corresponding to a particular size, a force is selectively induced for that size. This force was evaluated for a traveling wave [50], and further, the optical transport of semiconductor nanoparticles in a superfluid helium was demonstrated experimentally [53], wherein the frequency resonant with confined excitons was used for the incident beam. Moreover, the trapping of carbon nanotubes (CNTs) was theoretically demonstrated for standing waves at room temperature [52]. Because of the quantum mechanical properties of CNTs, they can be sorted and selectively trapped according to their diameter and chirality. The resonance radiation force could be useful not only for the quantum selective manipulation of nano-objects, but also for new types of sensing and microscopy techniques. A mechanical force can be induced between matter systems by irradiating them. If we utilize this mechanism for controlling the motion of a probe, it might be possible to develop radiation force microscopy that can be used to observe the spatial structure of the excited states of nanostructures [54, 55]. Thus, it is conceptually interesting that the resonant radiation force could link the microscopic degrees of freedom in nanostructures to their macroscopic degrees of freedom, which can enable us to access the quantum mechanical individualities of nanoparticles via non-contact approach.

1.3 Nonlinear resonant optical manipulation

Here, we should bear in mind that abovementioned resonance optical manipulations have been demonstrated for the transport of nanoparticles by using a traveling light wave, or trapping them by using a standing wave. How does the resonance effect work for the optical tweezers that is most commonly used technique for manipulating small particles? In fact, it can be shown by simple calculation that it is difficult to trap particles with a single resonant focused laser beam because the resonantly enhanced dissipative force strongly pushes particles away from the focal spot, thereby exceeding the gradient force used to trap them [56, 57]. However, recent experiments using resonance-focused laser beams have reported very positive results for molecular trapping and other such requirements [21, 22, 24, 25, 28, 30]. In addition, the results of these studies [21, 22, 25] exhibit certain puzzling phenomena that contradict the conventional interpretation of optical trapping based on the linear response theory [49, 56, 57]. For instance, two groups [21, 22] have successfully measured the optically biased diffusion of single organic molecules when a light source with a one-photon resonance frequency is made incident on the molecules. Curiously, the operated laser photon energy is reported to be above the maximum absorption energy of the single organic molecule in the experiment [21], although under normal conditions, trapping is possible only at energies below the resonance condition according to the conventional understanding of the trapping mechanism. Furthermore, the trapping force at energies above resonance [21] is several times stronger than that at levels below resonance for the
same molecule [22]. Likewise, a significant increase in the trapping time of fluorophore-labeled antibodies when using resonant laser light has been reported [25], wherein the antibodies are trapped in an energy region above the maximum absorption energy of the fluorophores. The demonstration conducted by Hosokawa et al. is more extreme; in their study, the trapping time was substantially increased by the addition of a resonant laser (at a wavelength of 532 nm) whose intensity was weaker by several orders of magnitude than that of the main nonresonant trapping laser (wavelength of 1064 nm) [24].

The key to understand these contradictions is nonlinear optical effects that are naturally induced by the high-intensity irradiation that is necessary to obtain sufficient radiation force for the trapping of nanoparticles [58, 59]. In particular, by considering each experimental condition, we coherently elucidate these puzzling phenomena by considering the effect of the nonlinear optical response beyond the perturbative regime. The demonstrations of nonlinear resonance optical manipulation not only explain the existing puzzling phenomena, but also open up the possibility of developing manipulation techniques with unconventional potential because the nonlinear optical response involves processes with considerably greater degrees of freedom than those of the linear optical response. For example, we propose a scheme to trap single organic molecules that is more effective than ever before [59, 60], to enable selective pulling of molecules with a particular transition energy [58–60], and our method can provide high-spatial-resolution optical manipulation beyond the diffraction limit [58, 59]. Moreover, we show the idea of resonant optical manipulation with the concept of coherent transient phenomena, which leads to, in particular, infrared and Terahertz optical manipulation with the coupling of Rabi oscillation.

On the other hand, recently, the trapping of metal nanoparticles using nonlinear effects has been reported [61]. Further, in a collaborative experiment group (in National Chiao Tung University Taiwan), they have reported the trapping of dye-doped polystyrene nanobeads by using the pulsed laser, that seems to be due to the two photon resonance which is one of the nonlinear resonance optical effect [62, 63] (this phenomenon cannot be observed by using CW laser). In order to investigate the field of the nonlinear resonance optical effect on optical trapping, we have conducted the experiment that the experimental situation is related to the report [63] as a collaborative research in Taiwan by ourself. As a result, we have found that, as an experimental fact, trapping behavior becomes efficient even with the CW irradiation. Although still the exact interpretation is under investigation, if we take into account the fact that there are several optical trapping experiments related to the nonlinear optical effects, the development of optical manipulation techniques under the heading of nonlinear response will become a reality in the near future.

In view of the abovementioned background of the study of resonant optical manipulation, in this thesis, we focus on the issue of how the inclusion of the idea of nonlinear optical response in optical manipulation can solve the conflict between conventional un-
understanding and recent experimental reports on molecular trapping by using a single laser beam. In addition, we propose a scheme to enhance the efficiency of molecular trapping by considering the nonlinear optical effect, and further, we examine the effect of the resonance optical binding force that is prominent when the density of nanoparticles within the focal spot increases. Further, we propose some unconventional optical manipulations by using the nonlinear resonance effect including, for instance, transient coherent phenomena and etc. Finally, we show the optical trapping of nanoparticles doped by dye molecule which can be two-photon excited by trapping laser. We believe that our approach can address the control of an increased number of degrees of freedom thereby enabling increased control to optically manipulate nano-objects, as historically, the inclusion of nonlinearity has greatly enhanced the potential of optical spectroscopy and photon manipulation.

1.4 Structure of this thesis

This thesis is organized as follows. In Chapter 2, we explain theoretical methods in detail to calculate the radiation force exerted on nanoparticles including the nonlinearity of the optical response. Results and discussions are provided after Chapter 2. In Chapter 3 we first demonstrate that the previous experimental results can be explained by the modeling of nonlinear optical manipulation via our analyses of several types of reported effects. In Chapter 4, we propose some unconventional optical manipulations based on the nonlinear optical response, such as optical pulling achieved using a traveling light wave and optical manipulation at with subwavelength resolutions. In Chapter 5, we propose the resonant optical manipulation utilizing the coherent transient phenomena. In particular, we suggest the idea of the pulling force using \( \pi \) pulsed lasers and the radiation force coupled with the Rabi oscillation. In Chapter 6, we propose the effect of resonance optical binding force on optical trapping that might make resonance optical trapping effective. In Chapter 7, we experimentally show the results of the optical trapping of the nanoparticles doped by dye-molecule which can be two-photon excited by trapping laser. Finally, in the Chapter 8, we provide our summary and outlook.
References


Chapter 2

Model and Theoretical Method

In this chapter, we first explain the calculation model used to describe optical manipulation. After describing the configuration of the laser beam and molecule and related parameters, we present the expression for the radiation force together with the equation for a tightly focused laser beam, and we derive the induced polarization. Finally, the method for determining a self-consistent field for nonlinear optical response is explained for the calculation of the resonance optical binding force.

2.1 Calculation model

Figure 2.1: Schematic of the focused beam and position of molecule assumed in the calculations. The molecule is fixed at position 1 and position 2 on the z-axis. Position 1 is closer to the side of the optical source far from the focal spot. At position 2 the gradient force becomes nearly maximum (z = +300 nm).

We assume that the light propagation and polarization are along the z- and x-axes, respectively, and the focal point is set to be the origin. For the calculation, we assume that the numerical aperture (N.A) of the oil-immersion objective lens used is 1.3 and that the focal length and incident beam diameter are 1.6 mm and 1.3 mm, respectively, as
indicated in Ref. [1]. In the calculation of the radiation force, we consider a molecule at two positions. Position 2 is located at \( z = 300 \) nm on the \( z \)-axis where the gradient force becomes nearly maximum. Position 1 is located on the negative side of the \( z \)-axis, and the distance from the origin is about ten times greater than that between the origin and position 2, where the gradient force toward the focal center becomes sufficiently weak. Regarding the target of the manipulation, we consider a typical organic molecule. Detailed energy diagrams are represented in the first part of each subsection after Section 2, corresponding to each model of the molecule used. As for the parameters of the dephasing constants of the molecular excited states and the background dielectric constant of the molecules, their values are uncertain. Therefore, we examine these values within a certain range. Further, we employ the high-frequency dielectric constant of water (a value of 1.77 is used in the present calculation) because the radius \( a \) of the organic molecule \((a = 1 \) nm) is one order of magnitude larger than that of the water molecule; our assumption is hence reasonable. Also the influence of a solvation shell (consisting of high concentration water molecule) surrounding around the target molecule to the polarizability, should be small, because the dielectric constant of the high density water molecule is almost the same as that of the normal water under the atmosphere pressure [2].

2.2 Radiation force for continuous wave laser

From the Lorentz force equation, the time-dependent radiation force \( \mathbf{F}(t) \) exerted on neutral matter is expressed as [3, 4],

\[
\mathbf{F}(t) = \int_V dr \left[ -\nabla \cdot \mathbf{P}(\mathbf{r}, t) \right] \mathbf{E}(\mathbf{r}, t) + \frac{1}{c} \frac{\partial \mathbf{P}(\mathbf{r}, t)}{\partial t} \times \mathbf{H}(\mathbf{r}, t),
\]

(2.1)

where \( \mathbf{P}, \mathbf{E}, \mathbf{H}, \) and \( c \) denote the induced polarization, electric fields, magnetic fields, and speed of light, respectively. The index \( V \) denotes the volume integral over the particle volume. We assume a time-harmonic continuous wave (cw) with frequency \( \omega \) throughout the calculations, i.e. \( \mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, \omega) e^{-i\omega t} \), and therefore, the equation for the radiation force can be written in a simple manner by taking the time-average as [3, 4],

\[
\langle \mathbf{F}(\omega) \rangle = (1/2) \text{Re} \int d\mathbf{r} [\nabla \mathbf{E}(\mathbf{r}, \omega)^\ast] \cdot \mathbf{P}(\mathbf{r}, \omega).
\]

(2.2)

Detailed expressions of the electric-field gradient and induced polarization are provided in subsections 2.4 and 2.5, respectively. (See the Appendix A for the derivation of the Eq. (2.2) from (2.1)) By substituting the real (imaginary) part of the polarizability into \( \mathbf{P} \) of Eq. (2.2), the gradient (dissipative) force can be separately defined. Besides, we should note that the frequencies of the electric field and the polarization should match for generating the radiation force.
2.3 Time dependent radiation force induced by pulsed laser

From the Eq. (2.1), the time dependent radiation force exerted on the target irradiated by traveling pulsed laser, is expressed as,

\[ F(z, t) = \int_V d\mathbf{r} P(z, t) \frac{\partial E_{\text{pulse}}(z, t)}{\partial x} \hat{x} + \mu_0 \frac{\partial P(z, t)}{\partial t} H_{\text{pulse}}(z, t) \hat{z}, \]  

(2.3)

where, \( E_{\text{pulse}} \) and \( H_{\text{pulse}} \) denote the electric field and the magnetic field of the pulsed laser propagating in \( z \)-direction. The directions of the polarization of the electric field and magnetic field are \( x \)-direction and \( y \)-direction, respectively. Expressions of them are indicated as,

\[ E_{\text{pulse}}(z, t) = E_{\text{pulse}0}(z, t) \exp[-i\omega t] \cdot \hat{x} + c.c., \]

(2.4)

\[ H_{\text{pulse}}(z, t) = H_{\text{pulse}0}(z, t) \exp[-i\omega t] \cdot \hat{y} + c.c., \]

(2.5)

\[ E_{\text{pulse}0}(z, t) = \frac{E_0}{2} \sqrt{\frac{2}{\pi}} \frac{1}{\sqrt{N}} \exp\left[\frac{-\sigma^2(z - ct)^2}{2c^2}\right] \exp[ikz] \exp[i\phi], \]

(2.6)

\[ H_{\text{pulse}0}(z, t) = \frac{E_0}{2} \sqrt{\frac{2}{\pi}} \frac{1}{\sqrt{N}} \frac{-\sigma^2(z - ct) + ik}{-\mu_0\left(\frac{\sigma^2(z - ct) - i\omega}{c}\right)} \exp\left[\frac{-\sigma^2(z - ct)^2}{2c^2}\right] \exp[ikz] \exp[i\phi], \]

(2.7)

\[ E_0 = \sqrt{\frac{2I}{\varepsilon_0 c}}. \]

(2.8)

Here, \( \sigma, N, k, \phi, I, \mu_0 \) and \( \varepsilon_0 \) are pulse width in frequency, repetition rate, wave number of the laser, phase, laser power, permeability of the vacuum and dielectric constant of the vacuum, respectively. With regard to the induced polarization and the partial differentiation of that in Eq. 2.3, are determined in Section 2.5.

2.4 Expression for tightly focused laser beam

For the calculation of the induced force, we assume a tightly focused laser beam as the incident light. We employ the angular spectrum representation to express the incident electric field as [5],

\[ \mathbf{E}(r, \omega) = \frac{ik}{2} \sqrt{\frac{n_1}{n_2}} E_0 \exp[-ikf] \begin{pmatrix} I_{00} + I_{02} \cos(2\varphi) \\ I_{02} \sin(2\varphi) \\ -2iI_{01} \cos(\varphi) \end{pmatrix}, \]

(2.9)

where \( n_1, n_2 \) denote the refractive indices of the target and solvent respectively, and \( f \) denotes the beam’s focal length. The wavenumber of the beam in the solvent is given
as, \( k = n_2k_0 \), where \( k_0 \) denotes the wavenumber in vacuum and \( \varphi = \cos^{-1}(x/\eta) \), and \( \eta = \sqrt{x^2 + y^2} \). The terms \( I_{00}, I_{01}, \) and \( I_{02} \) are described as,

\[
I_{00} = \int_{0}^{\theta_{\text{max}}} f_{\omega}(\theta) \sqrt{\cos \theta \sin \theta (1 + \cos \theta)} J_0(k\eta \sin \theta) \exp(ikz \cos \theta) d\theta,
\]

(2.10)

\[
I_{01} = \int_{0}^{\theta_{\text{max}}} f_{\omega}(\theta) \sqrt{\cos \theta \sin^2 \theta} J_1(k\eta \sin \theta) \exp(ikz \cos \theta) d\theta,
\]

(2.11)

\[
I_{02} = \int_{0}^{\theta_{\text{max}}} f_{\omega}(\theta) \sqrt{\cos \theta \sin \theta (1 - \cos \theta)} J_2(k\eta \sin \theta) \exp(ikz \cos \theta) d\theta,
\]

(2.12)

where \( \theta_{\text{max}} = \sin^{-1}(NA/n_o) \). The parameters \( NA \) and \( n_o \) denote the numerical aperture and the refractive index of oil (1.52), respectively, because we assume the use of an oil-immersion objective lens. The factor \( f_{\omega} \) is expressed as

\[
f_{\omega}(\theta) = \exp\left(-f_0^2 \sin^2(\theta)/\omega_0^2\right).
\]

We set \( \omega_0 \) to be equal to the diameter of the incident laser beam. The factors \( J_0, J_1, \) and \( J_2 \) denote the first, second, and third order Bessel functions of the first kind, respectively. The expression of the gradient of electronic field which is necessary to calculate the radiation force is given in the Appendix B.

### 2.5 Derivation of polarization including higher order contributions

In order to calculate the induced polarization under the condition of the high laser intensity required to trap single organic molecules, we solve the standard type of matter density matrix equations using a non-perturbative method. The density matrix equations including the phenomenological damping constants \( \Gamma \) are written as

\[
\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho] - \Gamma \rho,
\]

(2.13)

where \( \rho \) denotes the density matrix of the system, and the Hamiltonian \( H \) is represented as \( H = H_0 + V \). Here, \( H_0 \) denotes the unperturbed component and \( V \) denotes the light—molecule interaction energy, which is given by \( V = -\vec{\mu} \cdot \mathbf{E}(r, t) \), where \( \vec{\mu} \) denotes the dipole moment matrix. In this calculation, we restrict the energy level scheme of the target molecule to the three-level system with levels labeled 1, 2, and 3 in order from the low energy state. Thus, \( \vec{\mu} \) can be written in the \( 3 \times 3 \) matrix form as

\[
\vec{\mu} = \begin{pmatrix}
\vec{\mu}_{11} & \vec{\mu}_{12} & \vec{\mu}_{13} \\
\vec{\mu}_{21} & \vec{\mu}_{22} & \vec{\mu}_{23} \\
\vec{\mu}_{31} & \vec{\mu}_{32} & \vec{\mu}_{33}
\end{pmatrix}
= \begin{pmatrix}
0 & \vec{\mu}_{12} & \vec{\mu}_{13} \\
\vec{\mu}_{21} & 0 & \vec{\mu}_{23} \\
\vec{\mu}_{31} & \vec{\mu}_{32} & 0
\end{pmatrix}.
\]

(2.14)

Here, the off-diagonal elements \( \mu_{nm} \) denote the transition dipole moments between the levels \( n \) and \( m \), and the diagonal elements \( \mu_{nn} \) denote the permanent dipole moments of
level $n$ which are assumed to be zero in the present study. As for the $E$ of the incident fields, we consider up to two kinds of frequencies, namely $E_1(r, t) = E_1(r, \omega_1) \exp(-i\omega_1 t) + E_2(r, \omega_2) \exp(-i\omega_2 t) + c.c.$ Here, $(E_1, \omega_1)$ and $(E_2, \omega_2)$ denote the amplitude and frequency of the first and second beams, respectively. For this calculation, we approximate the total Maxwell fields by the incident field because the effect of the scattered fields is negligible in this case. Although a self-interaction via the scattering fields causes a radiative correction (shift and width), these effects are negligible for the radiation force exerted on molecules because the effects are very small. Moreover, the scattering from a molecule is almost isotropic and sufficiently small. Thus, an insubstantial amount of force is exerted by the scattering light. More detailed explanations regarding the validity of this treatment are elucidated in the Supplemental Material of our previous study [6].

The motion equations of each density matrix element can be written as

$$\frac{\partial \rho_{nm}}{\partial t} = (-i\Omega_{nm} - \gamma_{nm})\rho_{nm} - \frac{i}{\hbar} \left( V_{nm}(\rho_{mn} - \rho_{nm}) + V_{nl}\rho_{lm} - \rho_{nl}V_{lm} \right), \quad (n \neq m, l \neq n, m),$$  

$$\frac{\partial \rho_{nn}}{\partial t} = -\frac{i}{\hbar} \left( V_{nm}(\rho_{mn} - \rho_{nm}) + V_{nl}(\rho_{ln} - \rho_{nl}) \right) + \sum_{p>n} \Gamma_{pn}\rho_{pp} - \sum_{p<n} \Gamma_{np}\rho_{nn},$$  

$$\quad (n \neq m, l m \neq l p = 1, 2, 3),$$

where $\Omega_{nm}$, $\gamma_{nm}$, and $\Gamma_{nm}$ denote the transition energy, phase decay constants and population decay constants between levels $n$ and levels $m$, respectively. The light-molecule interaction energy $V_{nm}$ can be represented as

$$V_{nm} = -\vec{\mu}_{nm} \cdot \vec{E}.$$  

(2.17)

In the calculation, we note the conservation rule,

$$\rho_{11} + \rho_{22} + \rho_{33} = 1.$$  

(2.18)

Referring to Ref. [7], we expand the off-diagonal elements of the density-matrix in a Fourier series of the form

$$\rho_{nm}(r, t) = \sum_{j,k} \rho_{nm}^{(j,k)}(r, \omega_1, \omega_2) \exp[-i(j\omega_1 + k\omega_2)t] + c.c.$$  

(2.19)

where $j, k$ denote integers from -2 to 2. We ignore $|j|, |k| = 3$ and larger because their contributions to the force are very small for the condition under consideration. For example, $\rho_{nm}^{(0,1)}$ denotes the amplitude of density matrix elements oscillating in phase with beam 2. The diagonal elements are limited to the lowest order in the same expansion. Substituting Eqs. (2.17) and (2.19) into Eqs. (2.16) and (2.17) and using Eq. (2.18), we can derive the
density matrix equations for each frequency component along with the respective matrix elements in the form of the following generalized expressions.

\[ \frac{\partial}{\partial t} \rho_{nm}^{(j,k)} = (-i\Omega_{nm} + i\omega_1 + i\omega_2 - \gamma_{nm}) \rho_{nm}^{(j,k)} \]

\[ + \frac{i}{\hbar} \mu_{nm} \cdot \left( \mathbf{E}_1 (\rho_{nm}^{(j-1,k)} - \rho_{nm}^{(j-1,k-1)}) + \mathbf{E}_1^*(\rho_{nm}^{(j+1,k)} - \rho_{nm}^{(j+1,k-1)}) \right) \]

\[ + \mathbf{E}_2 (\rho_{nm}^{(j,k-1)} - \rho_{nm}^{(j,k)}) + \mathbf{E}_2^* (\rho_{nm}^{(j,k+1)} - \rho_{nm}^{(j,k+1)}) \]

\[ - \frac{i}{\hbar} \mu_{nl} \cdot \left( \mathbf{E}_1 \rho_{nl}^{(j-1,k)} + \mathbf{E}_1^* \rho_{nl}^{(j+1,k)} + \mathbf{E}_2 \rho_{nl}^{(j,k-1)} + \mathbf{E}_2^* \rho_{nl}^{(j,k+1)} \right) \]

\[ - i \hbar \mu_{lm} \cdot \left( \mathbf{E}_1 \rho_{lm}^{(j-1,k)} + \mathbf{E}_1^* \rho_{lm}^{(j+1,k)} + \mathbf{E}_2 \rho_{lm}^{(j,k-1)} + \mathbf{E}_2^* \rho_{lm}^{(j,k+1)} \right) \]

\[ \quad (n \neq m \ n > m \ l \neq m, n), \tag{2.20} \]

\[ \frac{\partial (\rho_{nm}^{(0,0)} - \rho_{11}^{(0,0)})}{\partial t} = \]

\[ - \frac{i}{\hbar} (2\mu_{n1} \cdot \left[ \mathbf{E}_1 \rho_{n1}^{(-1,0)} + \mathbf{E}_1^* \rho_{n1}^{(1,0)} + \mathbf{E}_2 \rho_{n1}^{(0,-1)} + \mathbf{E}_2^* \rho_{n1}^{(0,1)} \right. \]

\[ \left. \quad - \mathbf{E}_1 \rho_{1n}^{(-1,0)} - \mathbf{E}_1^* \rho_{1n}^{(1,0)} - \mathbf{E}_2 \rho_{1n}^{(0,-1)} - \mathbf{E}_2^* \rho_{1n}^{(0,1)} \right) \]

\[ - \mu_{mn} \cdot \left[ \mathbf{E}_1 \rho_{mn}^{(-1,0)} + \mathbf{E}_1^* \rho_{mn}^{(1,0)} + \mathbf{E}_2 \rho_{mn}^{(0,-1)} + \mathbf{E}_2^* \rho_{mn}^{(0,1)} \right. \]

\[ \left. \quad - \mathbf{E}_1 \rho_{nm}^{(-1,0)} - \mathbf{E}_1^* \rho_{nm}^{(1,0)} - \mathbf{E}_2 \rho_{nm}^{(0,-1)} - \mathbf{E}_2^* \rho_{nm}^{(0,1)} \right) \]

\[ + \mu_{m1} \cdot \left[ \mathbf{E}_1 \rho_{1m}^{(-1,0)} + \mathbf{E}_1^* \rho_{1m}^{(1,0)} + \mathbf{E}_2 \rho_{1m}^{(0,-1)} + \mathbf{E}_2^* \rho_{1m}^{(0,1)} \right. \]

\[ \left. \quad - \mathbf{E}_1 \rho_{1m}^{(-1,0)} - \mathbf{E}_1^* \rho_{1m}^{(1,0)} - \mathbf{E}_2 \rho_{1m}^{(0,-1)} - \mathbf{E}_2^* \rho_{1m}^{(0,1)} \right) \]

\[ + \sum_{p>n} \Gamma_{np} \rho_{np}^{(0,0)} - \sum_{p<n} \Gamma_{pn} \rho_{pn}^{(0,0)} - \Gamma_{21} \rho_{22}^{(0,0)} - \Gamma_{31} \rho_{33}^{(0,0)}, \quad (n, m = 2, 3 \ n \neq m \ p = 1, 2, 3), \tag{2.21} \]

The rest of the elements are obtained by using the relation \( \rho_{nm}^{(k,l)} = \rho_{nm}^{(-k,-l)} \). We use the steady state approximation and solve the simultaneous equations using Eqs. (2.20) and (2.21) to obtain the density matrix elements. Finally, we calculate \( \mathbf{P} = \text{Tr} \ < \rho \hat{\mu} > \) under the given excitation intensity. By these calculations, we can obtain the induced polarization \( \mathbf{P} \) under the strong laser intensity condition beyond the perturbative regime.

For the background polarization, \( \mathbf{P}_b = a_{CMRR} \mathbf{E}(r, \omega) \), we use the Clausius—Mossotti
law including the radiation reaction effect as \([8, 9]\),

\[
a_{CM} = 4\pi r^3 \epsilon_0 \epsilon_2 \frac{m - 1}{m + 2},
\]

(2.22)

\[
a_{CMRR} = \frac{a_{CM}}{1 - ik^3 a_{CM} \frac{6\sigma_0 \epsilon_2}{m}}
\]

(2.23)

where \(m = \epsilon_1 / \epsilon_2\) and \(\epsilon_1\) and \(\epsilon_2\) are dielectric constants of the molecule and surroundings, respectively. The value \(a_{CM}\) denotes the polarizability derived from the Clausius—Mossotti law alone, whereas \(a_{CMRR}\) denotes that including the effect of radiation reaction. By using \(a_{CMRR}\), we can calculate the dissipative force and the gradient force using a single calculation, instead of calculating the dissipative force using absorption and the scattering cross section and the gradient force only using \(a_{CM}\). On the other hand, variance of local material dielectric constant due to a laser heating of molecule and subsequent dissipation into the surroundings is negligible, because the temperature elevation on the molecule is estimated to be several mK by the calculation according to the literature \([10]\).

### 2.6 Self-consistent field in nonlinear optical response

Here, we demonstrate a method to determine the self-consistent fields including the nonlinear optical response in the region beyond the perturbative regime for the discussion of the resonance optical binding force. By using a dyadic Green’s function involving both the longitudinal and transverse fields in free space, the self-consistent field \(\mathbf{E}^s\) can be expressed as,

\[
\mathbf{E}^s(r, \omega) = \mathbf{E}(r, \omega) + \int \frac{d\mathbf{r}'}{4\pi} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{P}(\mathbf{r}', \omega)
\]

(2.24)

where the explicit expression of \(\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)\) is

\[
\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\exp[ik|\mathbf{R}|]}{|\mathbf{R}|} \left[ k^2 \mathbf{I} - \left( \frac{1 - i k |\mathbf{R}|}{|\mathbf{R}|^2} \right) \mathbf{I} + \left( \frac{3 - 3 i k |\mathbf{R}| - k^2 |\mathbf{R}|^2}{|\mathbf{R}|^4} \right) \mathbf{R} \mathbf{R} \right],
\]

(2.25)

where \(\mathbf{I}\) and \(\mathbf{R}\) denote the unit tensor and distance between \(\mathbf{r}\) and \(\mathbf{r}'\), respectively. Because of the higher-order contributions of nonlinear polarization, it is difficult to analytically solve the self-consistent field. Thus, we use an iterative method to solve the equations.
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Chapter 3

Elucidation of underlying discrepancies between experiments of resonance trapping and conventional theories

In this chapter, before we address the demonstrations of the nonlinear cases, we first show the results for a simple two-level system to recall the conventional understanding of laser trapping according to the standard linear response theory. Subsequently, we discuss how introducing the nonlinear elements resolves the contradictions between the existing understanding and the recent experimental results.

3.1 Two-level model

In the following calculations, we consider simple two-level molecules and limit ourselves to the linear response regime. Figure 3.1 shows the photon-energy dependence of the radiation force along the $z$-direction. The shapes of the radiation force spectra in Fig. 3.1(a) calculated for a molecule located at position 1 are almost the Lorentzian type that correspond to the shapes of typical absorption spectra. In other words, the dissipative force pushing the particles forward to the focal spot is dominant compared with the gradient force under the present condition, because the resonantly enhanced dissipative force is greater than that of the gradient one. For a molecule located at position 2, the spectral profile of the radiation force is almost the same as that at position 1. This leads to difficulty in trapping the particles by resonant light because the resonantly enhanced dissipative force is very strong even though near the focal spot is the optimum location to
Figure 3.1: Photon-energy dependence of the radiation force along the z-direction for several values of the dephasing constant (0.2 meV, 2 meV, and 20 meV). A molecule with two levels (see inset of (c)) is assumed. Figures 2 (a) and (b) correspond to positions 1 and 2, respectively, under weak excitation (1 nW); (c) and (d) correspond to positions 1 and 2, respectively, under strong excitation (1 mW). The inset of (b) is an enlarged view around the zero point of the vertical line. Thin solid black lines indicate the nonresonant case.
trap particles for the conventional nonresonant optical tweezers. However, if we examine the spectrum carefully, we find a region just below the resonance energy where the gradient force becomes dominant (see the inset of Fig. 3.1(b)). This feature was pointed out by Agayan et al. [1]. This is because the width of the dispersive spectral line is wider than that of the Lorentzian one. It should be noted that the former and the latter are related to the gradient and the dissipative force, respectively. When we use a laser with energy below the molecular resonance, the electric field and induced polarization are in phase, and thus, the gradient force is attractive at the focal spot, which is called “red-tuned trapping.” (In reverse, when the laser is tuned to the region above the resonance energy, their phase relation becomes inverse and the gradient force becomes a repulsive force.) However, for the present linear optical response regime, the absolute magnitude of the radiation force is too weak for trapping the molecules. Moreover, the frequency region over which the attractive gradient force is dominant is narrow and it is always associated with a very large peak of the dissipative force. This situation is not favorable to trap molecules because the molecules are easily pushed away from the focal spot if their resonance energies dynamically fluctuate.

Next, we consider the strong excitation regime wherein the optical nonlinearity appears (Figs. 3.1(c), (d)). For the molecule located at position 2, as the laser intensity increases, the Lorentzian line shape gradually changes to the dispersion type. In other words, the contribution of the gradient force to the total radiation force becomes dominant in the nonlinear regime because of the optical saturation effect that is related to the strong broadening of the spectral line. This situation is explained as follows: In the linear response regime, the growth rates of the dissipative force and the gradient force with the incident intensity are identical. However, in the nonlinear regime, their growth rates decrease due to optical saturation, and in particular, the growth rate of the dissipative force quickly decreases as compared with that of the gradient force, and finally, the former’s contribution vanishes. In this situation, the nonlinear polarizability is remarkably increased, but with the sign opposite to the linear one, and they are almost cancelled each other. This means that the absorption becomes saturated, and so does the dissipative force. This phenomenon is well-understood in the laser cooling technique [2]. On the other hand, the gradient force can increase even in this regime. Therefore, the entire line shape changes to the dispersion type. At position 1 that is far from the focal spot, the contribution of the dissipative force is still dominant because the gradient of the field is not very strong and the laser intensity in itself is not very strong. However, the resonant effect makes the force considerably stronger than that in the nonresonant condition. This leads to the expectation that molecules with resonance energy near the incident energy could be easily pushed forward to the focal spot, which might lead to an increase in molecular density near the focal spot as compared with the nonresonant case. We call this the resonance-drifting effect [3]. Although this is not a
case of resonant irradiation, a recent study has reported a similar effect wherein a strong dissipative force exerted on gold nanoparticles pushes them to the focal spot, and an area vacant of gold nanoparticles is found upstream of the focused laser beam [4].

Next, we explain how the abovementioned puzzling phenomena observed in recent experiments can be elucidated one by one when we extend the number of energy levels to consider a more realistic energy-level scheme of molecules. These two-level model studies aid in understanding the following discussions.

### 3.2 Trapping using blue-tuned laser

Considering the typical molecular energy levels consisting of vibrational levels and applying a high incident intensity sufficient to excite the molecules to the region of nonlinear optical response, we elucidate common mechanism underlying the contradiction between the results of theoretical studies under linear optical response and the experimental results with resonance optical tweezers. For the energy diagram of targeted molecules, we assume three energy levels including the vibrational excited levels, as illustrated in the inset of Fig. 3.2(a). This representation is assumed to be the energy-level scheme of rhodamine that is used in experiments [5, 6]. For the parameters for the dipole moment \( \mu \) and resonance energies \( \hbar \omega \) of the molecule, we choose the values according to the type of molecules chosen. We assume population decay times for the 3-2 state transition and the 2-1 state transition as 3 ps and 4 ns, respectively (that of the 3-1 state transition is ignored) [7, 8]. First, we consider the region of linear optical response. As discussed in a former subsection, the dissipative force plays a dominant role in the linear optical response regime (see Figs. 3.2(a) and (b)). However, in the nonlinear optical response regime, the role of the dissipative force is drastically changed. Figure 3.2(d) illustrates the radiation force spectra for the molecule located at position 2. There appears a dip structure above the 2-1 transition energy, namely, the gradient force becomes maximum in the higher-energy region. In addition, it should be noted that the radiation force in the higher-energy region is several times larger than that in the lower-energy region. In their experimental studies, Chirico et al. have reported that the trapping potential of Rhodamine 6G at higher energy levels (demonstrated by Osborne et al. [5]) was four times greater than that at lower energy levels (investigated by Chirico et al. [6]) (remark 1). In Fig. 3.2(d) the laser energies employed in each experiment are indicated by arrows above and below the 2-1 transition energy, and it is clear that the radiation force in the higher-energy region is approximately twice that in the lower-energy region. Moreover, the photon energy of the laser used in the experiment [9] lies between the energies of the 2-1 and 3-1 transitions if we assume that the vibrational-state gap (3-2 energy gap) is about 0.1 eV (remark 2). The remark 1 and 2 are all due to inverted population in the
Figure 3.2: Photon-energy dependence of the radiation force along the $z$-direction for several values of dephasing constant (0.2 meV, 2 meV, and 20 meV). A molecule with vibration levels (see inset of (a)) is assumed. Figures 3(a) and (b) correspond to positions 1 and 2, respectively, under weak excitation (1 nW); (c) and (d) correspond to positions 1 and 2, respectively, under strong excitation (1 mW). Thin solid black lines indicate the nonresonant case. The 2-1 and 3-1 transition energies are indicated by arrows in (c). Likewise, photon energies employed in the experiments of Ref. [5] and Ref. [6] are indicated in (d).
first excited state. In general, upon only considering the two-level scheme, a repulsive gradient force appears in the higher-energy region because of the antiphase relation between the electric field and the induced polarization. Thus, there is no attractive force above the energy corresponding to the maximum absorption. However, when the laser is sufficiently strong to generate population inversion, the phase of the polarization reverses, and therefore, the phase relation becomes in-phase in the higher-energy region. Further, Li et al. explain that, “All systems which have shown biased diffusion or trapping have been excited to the blue of the resonance” (remark 3) [9]. Moreover, Dienerowitz et al. state that, “The exact mechanism remains to be explored as the resonance effect shows molecule attraction into the high intensity region of the trapping laser even for blue-detuned traps” (remark 4) [10]. All the abovementioned issues are coherently elucidated by our proposed mechanism. Although the observed trapping efficiency and the magnitudes of the calculated trapping force cannot be directly compared, the calculated results in this study that uses realistic parameters for Rhodamine 6G correctly reproduce the essential profile of the experimental results discussed in the above experimental reports. As seen in Figs. 3.2(c) and (d), it is also interesting to note that the force spectra are not very sensitive to the dephasing constant in the strong nonlinear regime. This is because the peak width is primarily influenced by the saturation effect.

### 3.3 Proposal of two-color trapping scheme

On the basis of our calculations, in this section, we discuss a method to trap single organic molecules that could greatly improve existing methods by using two laser beams. Figure 3.3 illustrates the radiation force exerted on a single organic molecule as a function of its position along the $z$-axis. The thin solid blue line indicates the case when only a single beam is used. In this case, we select the optimum photon energy at which the gradient force becomes maximum in Fig. 3.2(d). We assume the dephasing constant to be 0.2 meV. The thick solid red line indicates the radiation force induced by using two-color beams. Here, it should be noted that the total incident intensity of the two-color beams is the same as that of the single beam. In comparison with the case of the single beam, the radiation force is amplified by a factor of several tens. This is due to the reduction in optical saturation in the two-beam case in comparison with the case of the single beam. In the single-beam case, two kinds of processes are involved. One is the generation of population inversion and the other is the stimulated emission. The optimum frequencies for these two processes are slightly different, for example, the former (latter) corresponds to the 3-1 (2-1) transition energy (see the inset of Fig. 3.2(a)). Even in the case of the single beam, it is possible to simultaneously initiate both the processes because the line width of the spectrum becomes sufficiently broad due to the effect of optical saturation. However, the
Figure 3.3: Spatial dependence of the radiation force along the $z$-direction. The zero point is the focal spot. The thin solid blue line shows the case of a single beam whose values are upscaled by a factor of 10. The thick solid red line indicates the case when a two-color beam of two slightly different colors is used. In both cases, we assume identical total incident intensities (1 mW), i.e., the intensity of each beam in the case of the two-color beam is 0.5 mW.

The radiation force becomes saturated, and it cannot increase linearly with the laser intensity. On the other hand, in the case of the present scheme, the two beams can be tuned to the abovementioned different transition energies, which reduces optical saturation, and thereby enhances the radiation force to a value greater than that in the case of single beam. Considering the fact that Osborne et al. [5] and Chirico et al. [6] succeeded in optically biasing the diffusion of single organic molecules, we believe our method can be used to truly “trap” single organic molecules. In practical application, lasers corresponding to 532 nm and 514.5 nm are available for the experiment, and therefore, we can confirm the feasibility of the present proposal if we prepare the dye molecules with an appropriate level scheme. It should be noted that considerably short relaxation times of the rotational and vibrational states for the molecules dissolved in a room-temperature solvent could make this method feasible though it seems difficult to apply this method to the cooling of molecules with few atoms because the relevant relaxation times are considerably longer than that of our target.

3.4 Pump probe trapping: Excited state absorption

Next, we investigate a phenomenon reported in Ref. [11] considering an excited-state absorption. In the experiment [11], two beams whose wavelengths are 532 nm and 1064
nm were employed; the 532-nm beam nearly corresponds to a wavelength of one photon resonance with dye that is doped in polystyrene beads. First, the authors observed a certain increase in the trapping time of dye-doped polystyrene beads upon increasing the intensity of only the 1064-nm laser up to 600 mW. Subsequently, the 532-nm laser was switched on. It is noteworthy, that the use of the second laser led to a drastic increase in the trapping time despite the fact that the 532-nm laser’s intensity was weaker than that of the main 1064-nm nonresonant laser by several orders of magnitude. For the theoretical analysis of this case, we calculate the radiation force using two beams (here, we use the terms “532-nm laser” and “1064-nm laser”) assuming the excited-state absorption shown in the inset of Fig. 3.4(a), namely, the 532-nm laser induces excitation from the second level to the third level under illumination by the 1064-nm laser. In the present demonstration, we treat a bare single molecule as the target in order to focus on the essential mechanism of the proposed effect. We assume dephasing constant of 0.2 meV and population decay times between the 3-1, 2-1, and 3-2 states as approximately 40 ns, 4 ns, and 3 ns, respectively. The aperture $\text{NA}$ is assumed to be 1.25 for these beams.

Figure 3.4 shows the two dimensional map of the radiation force as a function of the energies of the two laser beams. From this map, we can see that the trapping force becomes maximum in the lower-energy region of the 1064-nm laser. In this case, the 1064-nm laser is not resonant with the molecule in the absence of the 532-nm laser. However, in the presence of the 532-nm laser, cascade excitation by the 1064-nm laser becomes possible between the first and the second excited states because the 532-nm laser generates an excitation to the first excited state. Figure 3.5 shows the position dependence of the
radiation force for the optimum photon energies of the two lasers determined from the two-dimensional radiation force spectrum. From this result, we can see that the trapping force becomes approximately twice as large when the 532-nm laser with 2.4 \mu W of intensity is simultaneously applied together with the 1064-nm laser. This is particularly effective because the intensity of the assisting beam is three orders of magnitude weaker than the original trapping 1064-nm laser. Further we examine trapping at the intensity of 24 \mu W for the 532-nm laser. Although the increase in the radiation force with the intensity of the 532-nm laser is saturated (as seen in pink dashed line), if its intensity is sufficiently strong, we can say that this increase is very rapid as we need to add more 5 mW of the 1064-nm laser intensity if we want to double the magnitude of the radiation force solely by controlling the intensity of the 1064-nm laser. Further, if we consider the more realistic energy diagram including vibrational levels, the radiation force is expected to become large (compared to the same in the present three-level model) as the population of the first excited states is generated rapidly via vibrational levels. Although we require more detailed information regarding single molecular dephasing and the microscopic influences from the surrounding
water molecules for obtaining quantitatively accurate derivation of the radiation force, we can state that the above demonstrations (with reasonable assumptions) coherently elucidate the central profile of the existing experimental results. This result strongly suggests the potential of nonlinear optical manipulation to diversely extend the number of degrees of freedom to allow mechanical control of nano-objects.
References


Chapter 4

Unconventional optical manipulation based on nonlinear optical response

Thus far, we have summarized the essential physical mechanism underlying the recently reported experiments of resonant optical tweezers. The demonstrations in the previous chapter elucidate some puzzling effects in terms of nonlinear optical response, which certainly shows the existence of the nonlinear optical effect on the optical manipulation techniques. Therefore, in this chapter, we move on to demonstrating unconventional types of optical manipulation, which we term as “nonlinear resonant optical manipulation”, on the basis of our radiation force theory including nonlinear optical effects.

4.1 Stimulated recoil force

First, we demonstrate the “stimulated recoil force” that could be used to pull nano-objects using a traveling wave. The configuration of the laser beams and the nano-object under consideration are given in the inset of Fig. 4.1. Assuming the same energy levels of the particle as those shown in the inset of Fig. 3.2(a), we irradiated a particle with a standing wave to generate population inversion and we illuminated another laser beam along the direction perpendicular to the standing wave. The intensity of the lasers was 100 kW/cm$^2$; the polarization direction is assumed to be the same for these beams. In the absence of the pumping standing wave, the traveling wave exerts the usual dissipative force to push the particle (the thin blue line in Fig 4.1). However, under the strong irradiation of the standing wave, the direction of the force reverses. In this event, two photons with the same mode as the incident one are emitted via stimulated emission, and
hence, the momentum conservation law requires the particle to have a momentum opposite to that of the incident photon. With regard to the pulling force, there are many studies based on different mechanisms [1–9]. For instance, O. Brzobohatý et al. experimentally succeeded in the sizewise separation of micron-sized polystyrene beads by using a Bessel beam that ideally does not have a gradient force along the propagation direction. When the condition that forward-scattering overcomes back-scattering is satisfied, the particles are pulled upstream of the Bessel beam. However, there are no other cases that are based on the nonlinear optical response of the object being pulled which is our proposal, and the present demonstration indicates that quantum mechanical effects greatly increase the potential of optical manipulation. Further, the “pulling” operation clearly raises the number of degrees of freedom that can be addressed to manipulate small particles as compared with the “pushing” operation.

4.2 Sorting of single organic molecules

Next, we propose a possible application of the stimulated recoil force to sort molecules according to their energy levels. Figure 4.2(a) shows the assumed configuration of lasers and single organic molecules for the sorting operation. First, we irradiate the molecules with a standing wave, \( \mathbf{E}_1(\mathbf{r}, \omega_1) = E_1(\exp(ik_1x) + \exp(-ik_1x))\hat{y} \), to create a population inversion, and subsequently, these molecules are also irradiated by the traveling wave,
Figure 4.2: (a) Schematic of configuration of lasers and molecules for the demonstration of sorting single organic molecules by the use of the pulling force (stimulated recoil force). (b) Spatial dependence of the radiation force along the direction of the standing wave ($x$-direction). The thick blue line and thin red line indicate the results for two kinds of molecular transition energies (indicated in the graph). The transition energy for the case of the thick blue line is the same as that discussed in the previous section. On the other hand, in the case of the thin red line, the excited states are shifted downward by 0.1 eV. The thin red line values are multiplied by a factor of $10^2$. The intensities of both the traveling wave and standing wave are $10$ MW/cm$^2$, respectively. The negative variation in the force indicates a pulling event.

$E_2(r, \omega_2) = E_2 \exp(ik_2 z)\hat{y}$, whose wave vector $k_2$ is perpendicular to the wave vector $k_1$ of the standing wave, which leads to stimulated emission. The parameter $\hat{y}$ denotes the unit vector along the $y$-direction. The photon energies of the standing and traveling waves are $\hbar \omega_1 = 2.46$ eV and $\hbar \omega_2 = 2.36$ eV, respectively. In this process, the molecules absorb one photon and emit two photons via stimulated emission. Thus, according to the law of momentum conservation, the molecules are pulled toward the source of the traveling wave. Figure 4.2(b) shows the spatial dependence of the radiation force in the direction of the standing wave, wherein we observe that the magnitude of the pulling force becomes significant only in the high-intensity region of the standing wave due to population inversion. Further, we examine the difference in the radiation force for molecules with two different energy-level schemes; figure 4.2(b) indicates the possibility of sorting molecules according to their energy-level schemes. When we assume the same level scheme as that in the inset of Fig. 3.2(a), the single organic molecules are pulled toward the source of the traveling wave. On the other hand, for molecules whose excited levels are shifted
downward by 0.1 eV, the exerted force becomes a pushing force as in the normal case. This is because the molecule is resonant with the traveling wave but not resonant with the standing wave, which is the important condition to create population inversion. It should be noted that the radiation force in this case is considerably weaker than that indicated in thin red (in the figure) because of the optical saturation effect. In this manner, it is possible to draw away certain kinds of molecules from an assembly including different kinds of molecules in a solvent by using nonlinear resonant laser manipulation. The pulling force for the particles in the Rayleigh scattering regime is peculiar to the nonlinear resonant laser manipulation, and the above type of clear sorting cannot be realized by means of the normal pushing operation.

4.3 Subwavelength optical manipulation

![Figure 4.3: Spatial map of the radiation force in the radial direction in the xy plane induced by the 532-nm and 1064-nm laser beams. We centered the 1064-nm laser beam at (x,y) = (0,0) and centered the 532-nm laser beam at (0,0) (a) and at (-600 nm,0) (b). The arrows represent the direction of the radiation force.](image)

In this section, we demonstrate subwavelength optical manipulation, wherein the spatial region where the radiation force is prominent becomes narrower than the operating laser’s wavelength. The same kind of molecule as that shown in Fig. 3.3 is the trapping target. Figure 4.3 represents the two-dimensional spatial dependence of the radiation force within the xy-plane. In Fig.4.3(a), the focal centers of the 532-nm laser and 1064-nm laser are the same; the width of the major area where the radiation force is large in Fig. 4.3(a)
very nearly corresponds to the wavelength of the 532-nm laser. This major space shrinks when we move the those focal centers appropriately. In Fig. 4.3(b), we can see that the area of the prominent force becomes narrower than that in Fig. 4.3(a), wherein we select the optimum energy of the two beams. As the extra force from the assisting beam works only in the beam overlap area, we can provide a method to realize “subwavelength laser manipulation” beyond the diffraction limit without using the near field optical force [10]. This mechanism is based on a concept similar to that of ultra-resolution optical microscopy [11, 12] using two beams.
References


Chapter 5

Optical manipulation with coherent transient phenomena

In this chapter, we introduce the concept of the coherent transient phenomena to the calculation of the radiation force by utilizing a pulsed laser which has a more capability to induce the optical nonlinearity compared with the case of CW irradiation. For instance for the case of 100 fs pulsed laser with 80 MHz repetition frequency, the amplitude of a temporal instantaneous laser intensity is about 5 order larger than laser intensity of the CW laser (an averaged input laser power is the same). In the following discussions, first we introduce the stimulated recoil force by using \( \pi \) pulsed lasers. Second, we consider the coupling between the polarization induced by the Rabi oscillation with the aid of a permanent dipole moment and a far infrared laser. Before introducing these mechanisms, we would like to emphasize that application of the resonant pulsed laser allows us to incorporate the concepts of the coherent transient phenomena into the manipulation scheme that is not accessible only by CW irradiation.

5.1 Stimulated recoil force using \( \pi \) pulsed lasers

Here, we extend the idea of the stimulated recoil force (Section 4.1) using \( \pi \) pulsed lasers, which is not necessary to assume the three-level model. Fig. 5.1 shows the configuration of the lasers and target. For the lasers, we assume two \( \pi \) pulsed lasers with 1 ps delay time. Both laser’s center photon energy, averaged intensity, pulse width, and repetition rate are 2.36 eV, about 1.2 W/cm\(^2\), 350 fs and 100 kHz, respectively. From these parameters, an instantaneous maximum intensity is estimated to be, 1.2 W/cm\(^2\) \times \frac{1}{100 \times 10^3} \times \frac{1}{350 \times 10^{-15}} = 33 \text{ MW/cm}^2 \) and these parameters are realistically available by using Spirit-OPA (Spectra Physics). In order to describe our idea clearly, both lasers are assumed to be simple traveling wave instead of assuming the focused beams. Practically, the first and second
Figure 5.1: Conceptual scheme of the stimulated recoil force by using \(\pi\) pulsed lasers and position of the lasers and target. Irradiation of the first \(\pi\) pulsed laser can create the population inversion and subsequent second \(\pi\) pulsed laser is used for stimulated emission. The propagating directions of the \(\pi\) pulsed lasers are perpendicular to each other and polarization directions are orthogonal to this page. This process allow us to pull the target toward to the upper stream of the second laser.

Lasers are used to create the inverted population and the stimulated emission, respectively. The propagating directions of the \(\pi\) pulsed lasers are perpendicular to each other and polarization directions are orthogonal to this page. In regard to the target, we assume the parameter of typical colloidal quantum dot, for example CdSe quantum dot, consisting of simple two levels, whose transition energy and transition dipole moment are 2.36 eV and 15 Debye, respectively. The time of the population and the phase decays are 4 ns and 3 ps, respectively.

Figure 5.2 (a) shows temporal dependence of the population of excited state. Due to the first \(\pi\) pulsed laser, the amplitude of the population becomes almost one corresponding to population inversion. Subsequently, the second \(\pi\) pulsed laser is applied to generate the stimulated emission. In this manner, population drops to the ground state. If we provide the interpretation by mean of the Optical Bloch Sphere picture, during the irradiation of two \(\pi\) pulsed lasers, Bloch vector is excited directly above and down to the ground state. As we see in the Fig. 5.2 (b), the first \(\pi\) pulsed laser pushes the target along the propagating direction of the first \(\pi\) pulsed laser. Then, the stimulated recoil force occur in connection with the stimulated emission due to the irradiation of the second \(\pi\) pulsed laser. In other words, this scheme can be used to pull and sort the certain kind of the target even the target has only two levels which is typically difficult to create the
Figure 5.2: (a) Excited state population of the target as a function of time. (b) Time
dependent radiation force induced by the first $\pi$ pulsed laser and the second one, respectively. 0 fs is the time when the first laser intensity becomes maximum and 1 ps is that for the second laser.
inverted population under CW irradiation. We believe that the usage of the $\pi$ pulsed lasers expand the variety of the target for pulling and sorting by using stimulated recoil force. Additionally, if we need to keep the target fixed in the direction of the first pulsed laser, we can use the standing wave instead of the traveling wave.

5.2 Coupled with Rabi oscillation

![Diagram of lasers and target relationship](image)

Figure 5.3: (a) Position relationship of the lasers and target. There are two pulsed lasers in order to induce the Rabi oscillation and to couple with the polarization caused by the Rabi oscillation with the help of permanent dipole moment, respectively. (b) Energy diagram of the target is consist of simply two levels.

Next, we introduce the mechanism to induce the radiation force that arises due to the interaction between polarization caused by the Rabi oscillation with the aid of the permanent dipole moment and the far infrared laser. A configuration of the lasers and the position of the target and assumed energy level scheme are indicated in Fig. 5.3.

We assume two lasers: a first pulsed laser is used to induce the Rabi oscillation and a second pulsed laser is used to couple with polarization caused by the Rabi oscillation. With respect to the first pulsed laser, the center photon energy, averaged intensity, pulse width, and reputation rate of the first pulsed laser are 2.36 eV, 450 W/cm$^2$, 350 fs, and
100 kHz, respectively. From these parameters, an instantaneous maximum intensity is estimated to be, $450 \text{ W/cm}^2 \times \frac{1}{100 \times 10^9 \times \frac{1}{350 \times 10^8}} = 13 \text{ GW/cm}^2$ and these parameters are realistically available by using Spirit-OPA (Spectra Physics). For the second pulsed laser, referencing from the paper [1], the wavelength, pulsed width, repetition rate and laser power are, 9 to 18 µm (69 meV to 140 meV), 140 fs, 88 MHz, and 1 µW, respectively. With regard to the laser beam’s diameter, we assume that to be 50 µm, which is experimentally possible by using the Zinc Selenide Infrared (IR) Focusing Objectives (Edmund Optics). Therefore, the averaged intensity and instantaneous maximum intensity are 51 mW/cm$^2$ and 4.1 kW/cm$^2$, respectively. The propagating directions of these two pulsed lasers are perpendicular to each other and polarization directions are orthogonal to this page.

With regard to the target, referencing the parameter of colloidal CdSe quantum dot, we assumed the transition energy and the transition dipole moment, $\mu_{21}$, as 2.36 eV and 15 Debye, respectively, and difference of permanent dipole moments between excited and ground states, $\mu_{22} - \mu_{11}$, as 32 Debye [2–4]. The time of the population and the phase decays are 4 ns and 3 ps.

In the following, one by one, we explain the mechanism of the radiation force arising due to the coupling of the Rabi oscillation. First of all, we need to induce the Rabi oscillation by irradiating the first pulsed laser. In this matter, as we see in Fig. 5.4 (a), population of the excited state oscillates reflecting the Rabi frequency. Usually for the atomic case, temporal oscillating population does not affect the polarization because they do not have the difference in the permanent dipole moments (static dipole moments) between excited state and ground state. However, for the molecule and the colloidal quantum dot [2–4] which have the difference in the permanent dipole moments, the Rabi oscillation affects the polarization. By considering the equation of the polarization which is expressed as, for the two-level model, $< P > = \rho_{21}\mu_{12} + \rho_{12}\mu_{21} + \rho_{11}\mu_{11} + \rho_{22}\mu_{22} = \rho_{21}\mu_{12} + \rho_{12}\mu_{21} + \rho_{22}(\mu_{22} - \mu_{11})$, it is easy to understand that there are the contribution of the permanent dipole moment to the polarization.

After preparing the polarization caused by the Rabi oscillation with the permanent dipole moment, we can induce the radiation force coupled with the Rabi oscillation by irradiating the second pulsed laser, if the frequencies of the Rabi oscillation and that of the second pulsed laser are the same. As a result of this scheme, the momentum caused by the second pulsed laser is shown in Fig. 5.4 (b) as a function of the photon energy of the second pulsed laser. The momentum is calculated by time integrating the time dependent radiation force for each photon energy of second pulsed laser. There is a signature peak around about 0.11 eV, corresponding to the Rabi frequency. As the laser intensity of the first pulsed laser is changing in time, the Rabi frequency is also changing in time, therefore, there are certain peaks appearing below the energy about 0.08 eV. The opposite direction of the radiation force appears around 0.08 eV, because of the phase relation between the
Figure 5.4: (a) Population of excited state as a function of time. 0 fs is the time when the instantaneous electric fields of the both pulsed laser become maximum. (b) Photon energy dependence of momentum calculated from the radiation force induced by IR laser. Thick red and thin blue lines denote the momentum without and with the $\lambda/2$ plate, respectively.
polarization and the second pulsed laser. It is notable that, if we change the phase of
the second pulsed laser by using the $\lambda/2$ plate, the sign of the radiation force becomes
reverse (thin blue line in 5.4 (b)). In the previous chapter, we use the same laser to induce
the polarization and to drive the polarization, therefore it was impossible to change the
sign of the radiation force by using the $\lambda/2$ plate, because we cannot change either phase
of polarization or laser. Namely, the phase relation of the polarization and the laser is
always fixed in the previous case. However, in present scheme, the roles to induce and drive
the polarization are separated by using two pulsed lasers, individually, therefore we can
control their phase relation, which can be used to change the sign of the radiation force.
Furthermore, this force is not exerted to the targets if they do not have the difference in
the permanent dipole moments, which means that it is possible to sort them according to
whether they have a permanent dipole moment or not.

On the other hand, since the Rabi frequency is controlled by the strenght of the cou-
pling electromagnetic field, there are theoretical proposal to use this scheme for frequency-
tunable Terahertz emission [5]. This advantage is also useful for our scheme of optical
manipulation, because it is possible to continuously tune the frequency of the polarization
which is resonance to the second pulsed laser. In other words, in an ordinary way, we
need to control the laser’s photon energy to resonate with the target, however, we can
control the resonance energy of the target by changing the intensity of the first pulsed
laser because the frequency of the polarization induced on the target is the same as the
Rabi frequency. Thus, we can prepare the resonance condition by controlling the intensity
of the first pulsed laser instead of tuning the wavelength of the laser. Additionally, we
would like to mention that, in principle, this scheme can be also applied to the region of
Terahertz frequency leading to Terahertz optical manipulation. Finally, if we need to keep
the target fixed in the direction of the first pulsed laser, we can use the standing wave
instead of the traveling wave.
References


Chapter 6

Resonant optical binding force

Figure 6.1: Two dimensional spatial distribution of the radiation force acting on a molecule in the presence of another molecule fixed at the focal center. Figure 6.1(a) and (c) represent the radiation force along the $x$-direction and $y$-direction, respectively. Figure 6.1(b) and (d) show the enlarged view of (a) and (c) near the center of the focal spot.
In the previous chapters, we have demonstrated how the consideration of the non-linearity of a target’s optical response can explain the recent positive effects observed in experiments on resonant molecular trapping, and also how this idea can be extended for application to unconventional optical manipulation. Although these explanations are successful, some other mechanisms that make resonant optical trapping effective might underlie the observed phenomena. As one of such possibilities, we discuss a possible resonance optical binding force (or interparticle resonance radiation force [1, 2]) that might play an important role when the interparticle distance becomes sufficiently short such that the binding force increases and becomes comparable with the direct radiation force. In order to calculate the interparticle force, we must consider the self-consistent field that has been neglected in the previous subsections.

In order to discuss the effect of the resonance optical binding force on molecular trapping, we calculate the radiation force exerted on a particle (particle A) near the focal spot in the presence of another particle (particle B) fixed at the center in the focal spot. To provide the essential insight into this effect, here, we simply assume the molecule to be a two-level system. Considering target is the same as the target which we assumed in Section 3.1. Figures 6.1(a) and (c) show the plot of the radiation force exerted on the particle A as a function of its position on the $x$$y$-plane. The contribution of the resonance optical binding force is negligible in this spatial region, but upon closer examination around near the focal spot, we find the contribution of the resonance optical binding force (Figs. 6.1(b) and (d)). This is due to the interparticle interaction via the longitudinal field (evanescent field) of the molecules. In this calculation, we fix the incident polarization to be along the $x$-direction, therefore, the characteristics of the radiation force are different according to whether it is along $x$-direction and $y$-direction. The attractive and repulsive forces arise because of anisotropy of the molecules. If the distance between two molecules is of the order of several nanometers, the optical binding force becomes two orders of magnitude larger than the direct radiation force. These results indicate the possibility of the increase in molecular density at the focal spot. Furthermore, the direction of the resonance optical binding force is related to light polarization, optical frequency, and the anisotropy of the molecules, and therefore, it might be possible to control and create particular forms of aggregated molecule structures by changing the properties of the incident light and the molecules.

In this manner, in the resonance condition, the optical binding force becomes sufficiently large to affect the motion of molecules if their density is high near the focal spot. Thus, the consideration of this effect in the analysis of resonant optical trapping could provide important information to understand the observed phenomena.
References


Chapter 7

Optical trapping of nanoparticles doped by dye molecule

Thus far, in Chapter 3, we have introduced the nonlinear resonant optical effects to the calculation of the radiation force, that successfully elucidates the interpretation of the puzzling phenomena of the resonant optical trapping experiments [1–4] contradicting the conventional understanding. However, considering all of these experimental reports did not aim to investigate the nonlinear resonant optical effects on the optical trapping, the real advantage of optical manipulation utilizing nonlinear resonance optical effects has not been maximized yet. Therefore, to maximize the ability of this technique, first, in Chapter 4, we have already proposed the nonlinear resonant optical manipulation that raises the number of degrees of freedom to control the nanoparticles such as the stimulated recoil force, the subwavelength optical manipulation, and etc. Secondly, in this chapter, we have addressed this purpose experimentally as described in the following.

Recently, from a collaborative experimental group (in National Chiao Tung University Taiwan), they have reported the results of the optical trapping that seem to be due to a two-photon resonance that is one of the nonlinear resonant optical effect [5, 6]. In particular, for the experimental method, they have monitored a trapping behavior by measuring the light intensity of a halogen lamp scattered from the trapped particles (dye-doped polystyrene nano-beads) which can be two-photon excited by using the trapping pulsed laser. As a result, this light intensity increases as the square of the laser power of the trapping pulsed laser, that indicates the number of the particles trapped at the focal spot also increases as the same tendency. It is notable that, this phenomenon cannot be observed by using the CW laser. Also when the polystyrene nano-beads are not doped by the dye, this tendency becomes linear from the square.

However, we operated the related experiment by ourself at the Masuhara laboratory in Taiwan, and in this chapter, we report the result that implies there are some difference
in trapping behavior between the doped one and the non-doped one, even with the CW irradiation. Note that, the dye and its concentration used in the experiment [6] are unknown because the dyes are commercial product, hence, we started from the preparation of the sample with well known dye (perylene).

In the following section, first of all, we explain the optical setup and sample preparation including the evaluation of the samples. Next, in order, we describe the trapping results measured by two different methods, discussion, conclusion, and future works.

7.1 Optical setup

![Schematic picture of the experimental setup based on an inverted microscope for optical trapping. Abbreviated names and detail are explained in the text of this thesis.](image)
Fig. 7.1 shows the schematic diagram of the experimental setup. For the trapping laser, 800 nm continuous wave (CW) laser from Ti:sapphire laser beam (Tsunami; Spectra Physics) is tightly focused by using the objective lens (NA=0.9) into the sample solution. By using a 800 nm dichroic mirror, laser beam is introduced to the objective lens. $\lambda/2$ plates with a beam splitter are aligned to control the laser power by rotating the fellow of the $\lambda/2$ plate. In this experiment, the power can be controlled up until 400 mW after the objective lens. Also the beam is collimated and expanded to 5 mm in diameter by a pair of positive lenses with focal length being 100 and 200 mm, respectively. Prism pair is placed after the Ti:sapphire laser for the femtosecond-pulse mode to compress the pulse duration. However in our present experiment, we only use the CW laser, because we have observed the unknown nonlinear signal from the sample under irradiation of the femtosecond laser pulses, that prevents to monitor the pure scattering light and pure two-photon fluorescence light as we explain later. Upper left of Fig. 7.1 is the picture of the sample chamber. The chamber is sandwiched by glass substrates and its thickness is 1 mm. All the three samples are put into the chamber, because we do not want to change the distance between the dark field condenser lens and the sample chamber. If the distance will be changed, we can’t compare the results between each sample, because the light intensity of the halogen lamp becomes different.

In order to measure the trapping behavior of nanoparticles, first, light scattering from the halogen lamp is observed by using Electron Multiplying Charge Coupled Device (EM CCD) camera incorporating the dark field condenser lens to obtain the signal from focal spot where the particles will be trapped. To avoid the one-photon excitation of the perylene dye molecule under the halogen lamp irradiation, we used the 532 nm long pass filter (LPF) to cut the wavelength shorter than 532 nm in wavelength. Besides, 750 nm short pass filter (SPF) and 633 nm LPF are used to remove the fundamental 800 nm laser and the two-photon fluorescence from the perylene, respectively. Thus we have observed the scattering light of the halogen lamp ranging from 633 nm to 750 nm.

Secondly, two-photon fluorescence emitted from the perylene that is two-photon excited by the 800 nm CW laser, is monitored by CCD-coupled polychromator (Princeton Instrument; SpectraPro2300i) passing through the optical fiber. During this measurement, both halogen lamp and room light are turned off. To capture the two-photon fluorescence from the focal spot, a pinhole is located before the CCD-coupled polychromator. Although the two-photon fluorescence intensity is very weak under the excitation of 800 nm CW laser, by increasing the exposure time up to 1 sec, it is possible to measure the two-photon fluorescence signal from the focal spot. Additionally, this two-photon fluorescence spectral shape is the same as the one-photon fluorescence, therefore, we can mention that trapped sample is not optically broken by the laser irradiation.

In the following section, by utilizing this optical setup, we show the optical trapping
results obtained by measuring the light scattering from halogen lamp and the two-photon fluorescence from the perylene dye molecule. These two individual monitoring methods will be allow us to discuss the trapping behavior from different angles.

### 7.2 Sample preparation

![Image of sample preparation](image)

Figure 7.2: An illustration showing how the perylenes are doped inside the polystyrene beads using the swelling process of polystyrene beads in the tetrahydrofuran solution.

Fig. 7.2 describes the schematic image of sample preparation. According to the method indicated in reference [7], we dope the perylene (Pe) to bare polystyrene (BPS) beads by using swelling of polystyrene beads in tetrahydrofuran (THF) solution. Hereafter, the doping method and the mechanism are explained. First of all, in order to make perylene doped polystyrene (PePS) beads, it is necessity to prepare the Pe solution dissolved in THF and BPS beads dispersed in water, individually. With regard to the former solution, here we prepared two different molar concentration of Pe solutions (in particular $3.63 \times 10^{-3}$ M and $3.63 \times 10^{-4}$ M), so as to control the number concentration of the Pe inside each BPS bead. With respect to the latter solution, we purchased the Polybead Microspheres 0.05μm from Polyscience Inc. (spherical polystyrene is formed by linear chain polystyrene: actual particle diameter and particles concentrations are 43 nm and $3.8 \times 10^{14}$ particles/ml, respectively). After mixing these solutions together, the BPS beads are swelled because the THF solution dissolve the BPS beads. Then, the Pe can diffuse into the vacant space of BPS beads because of the swelling of BPS beads. For the mixing process of these solutions, we used a Vortex Mixer for 10 min. Also mixing ratio of the Pe solution and the BPS beads solution is fixed to be 20 vol.% and 80 vol.%, respectively. In particular for our preparation, we add 800 μl and 200 μl for the BPS solution and the Pe solution, respectively. Note that, if the adding THF volume percentage is high enough, BPS beads are fused together, as a result of the aggregations. For example, when the adding THF is around 70 vol.%, we had found the aggregations that can be seen with the naked eye. Therefore, controlling the volume percentage of the THF solution
is very important to prepare the ideal sample, because the optical trapping potential is proportional to the cubes of the diameter. Next, in order to remove the THF solution, the mixture is diluted with water and centrifuge in the a centrifugation for at least 4 times. For the container of the sample solution, we use a centrifuge tube (Centriprep: Centrifugal Filters Ultracel YM-50 Regenerated Cellulose 50,000 MWCO) with the filter to keep the PePS beads inside the tube and push out the water-THF solution from the tube. Additionally, in this process, remaining Pe which is not doped into the BPS beads should removed with THF solution. Finally, we used the filter (Millipore: 13 mm Millex Filter 0.22 µm PVDF Non-Sterile) to remove the aggregations. According to this method, we prepared two PePS beads whose Pe concentrations are almost two times different, that are PePS 230 and PePS 457. The numbers 230 and 457 are the average perylene number inside the each BPS bead that are determined by using the absorption spectra of known concentrations of BPS beads in water and the Pe dissolved in THF solution. Actually, in the beginning, we prepared the Pe solution which molar concentration are 10 times different, however after determining the Pe concentration inside the each BPS bead was only about 2 times different. Hence, the preparing method may be needed to consider in the future work to control the Pe concentration in more wide range. Those particle concentrations are $1.35 \times 10^{13}$ particles/ml for both samples. Estimating from these particle concentrations, inter-particle distance, $1 \text{ cm}/\sqrt[3]{2.85 \times 10^{13}}$, is about 420 nm and the number of the particles inside the focal sphere (assumed to be 0.5 µm in radius), $\frac{4}{3} \pi (0.5\mu m)^3/(420 \text{ nm})^3$, is about 7 particles.

### 7.3 Evaluation of the prepared sample

In this section, we evaluate our sample by mean of a dynamic light scattering and excitation and emission spectroscopies. As a result, we have found that, there are no significant difference in size before and after the preparation. Moreover, we have confirmed that Pe is existing as a monomer in the BPS beads.

#### 7.3.1 Dynamic light scattering

Fig. 7.3 represents the diameter of the particles analyzed by using the dynamic light scattering. By comparing the each figure, the diameter is almost the same before and after the preparation. Note that there are aggregations which size is about 120 nm in diameter after the preparation (see the fig. 7.3 (b) and (c)). However, the ratio of the single particles number compared with the aggregated one is rather large, therefore we may mention that even after the preparation, most of the particles are existing as the single particles in the solution.
Figure 7.3: Particle number as a function of particle diameter obtained from the dynamic light scattering analyzer. (a), (b) and (c) are the samples BPS, PePS 230 and PePS 457, respectively. Mean diameters are 43 nm, 43 nm and 41 nm for the case of (a), (b) and (c), respectively. Note that there are aggregations in (b) and (c) and the percentages of the aggregations compared with the single particles are 2 % and 0.8 %, respectively.
7.3.2 Excitation and emission spectra

![Excitation and emission spectra of PePS 457 beads dissolved in water and an absorption spectrum of the Pe dissolved in the THF solution.](image)

Figure 7.4: Excitation and emission spectra of PePS 457 beads dissolved in water and an absorption spectrum of the Pe dissolved in the THF solution. The excitation spectrum is detected at the 505 nm in wavelength and the emission spectrum is excited at 400 nm in wavelength. The amplitude of these spectra is normalized.

Fig. 7.4 is the excitation and emission spectra of the PePS beads which we prepared. The shape of the excitation spectrum is the same to that of Pe in the THF solution (a dot blue line) except the slight shift of the peak positions to the long wavelength side because the surrounding characteristic of a polar is changed from THF solution to BPS beads. Thus, we can mention that the Pe is existing as the monomer inside the BPS beads.
7.4 Results

Here, we show the results of the trapping behavior by measuring the scattering of the halogen lamp and the two-photon fluorescence of the Pe molecule, respectively.

7.4.1 Scattering of the halogen lamp

Fig. 7.5 and 7.6 denote the time dependence of the light intensity scattered from trapped nano-particles under the illumination of the halogen lamp. Although we need to scrutinize the relation between the number of the particles and the scattering light intensity, here we assume that the scattering light intensity is linearly proportional to the number of the particles, because the size of the BPS beads is in the Rayleigh region [8]. We operate the experiment for the three samples, which are BPS, PePS 230 and PePS 457, changing the laser power from 50 mW to 400 mW by the step of 50 mW. Looking at the result of BPS, there are no signature rise curves in the whole laser power (see the top of the Figs. 7.5 (a) to (d) and 7.6 (e) to (h)). This means there are no obvious detectable trapping for the sample of BPS. However when we dope Pe to BPS beads, the behavior becomes different. Of course in the region of lower laser power (Figs. 7.5(a) and (b)) there are no rise curves for the whole sample, however when the laser power is higher than 150 mW, the scattering intensities are slightly rising with time for the doped samples (for example, see the scattering intensity at the 15 s). In other words, our experimental results indicate that dye doping to BPS beads makes the trapping efficient compared with the case of BPS beads. Especially, as we see in Fig. 7.6 (h), by comparing the rise curve of PePS 230 and PePS 457, the tendency of rise curve of PePS 457 is larger than that of the PePS 230, which indicates that the high concentration of the Pe makes the trapping more efficient. In contrast, in Fig. 7.5 (d), the scattering intensity of the PePS 230 is larger than the case of that of PePS 457, contradicting the matter in Fig. 7.6 (h). These problems are still under consideration, however even neglecting the Figs. 7.5 (d) and 7.6 (h), we can mention that doping effects make the trapping behavior more effective than the case of non-dopant.
Figure 7.5: Temporal dependence of the scattering intensity of the halogen lamp scattered from the focal spot. From (a) to (d), the power of the trapping laser is increased by the step of 50 mW ranging from 50 mW to 200 mW. Top, middle and under parts of the each figure denote the samples for BPS, PePS 230 and PePS 457, respectively.
Figure 7.6: Temporal dependence of the scattering intensity of the halogen lamp scattered from the focal spot. From (e) to (h), the power of the trapping laser is increased by the step of 50 mW ranging from 200 mW to 400 mW. Top, middle and under parts of the each figure denote the samples for BPS, PePS 230 and PePS 457, respectively.
7.4.2 Two-photon fluorescence

Fig. 7.7 indicates the time dependence of the two-photon fluorescence (TPF) intensities from the focal spot measured by the CCD-coupled polychromator. First of all, when the laser power is higher than around 200 mW for the both curves (PePS 230 and PePS 457), the TPF intensities increase with the passage of time, that indicates the nanoparticles are trapped at focal spot as similar to the results of the scattering measurement. Especially, if we look carefully at the case of 200 mW laser power, the curve of the PePS 457 is slightly increasing with the time, although that of PePS 230 is vibrating around the zero line. Additionally, the absolute heights of the PePS 457 are almost 2 times larger than that of PePS 230, that shows a good agreement with the difference between the Pe concentration of PePS 230 and PePS 457 ($457/230=1.99$).

However, at the present stage, we cannot clearly determine the relationship between PePS 230 and PePS 457, because the difference of the Pe concentration between PePS 230 and PePS 457 is only two times which range is too small. Therefore, in the future work, we need to operate the experiment in more wide range. Also we need to conduct the more experiment to determine the error bar.

To summarize the present results, although we cannot clearly show the relation between PePS 230 and PePS 457, we can say that, as an experimental fact, by means of two different measurements (the scattering and the TPF intensities), both PePS 230 and PePS 457 are trapped by the 800 nm CW laser. Beside, when the laser powers are 50 mW and 100 mW, the line curves are slightly decreasing with increasing the time, that maybe due to the heat effect of the solvent water (though the absorption of the 800 nm laser by water is very small) or an optical damage of the Pe (we leave these discussions in future work).
Figure 7.7: Temporal dependence of the two-photon fluorescence intensities collecting from the focal spot for the samples of PePS 230 and PePS 457, respectively.
7.5 Discussion

Following the previous experimental results, in this section, we attempt to consider and discuss three possibilities to give an interpretation for our experimental results.

7.5.1 Influence of non-resonant refractive index of perylene

Here, we estimate a total non-resonant refractive index of the PePS bead, that is the sum of the non-resonant refractive indices of the BPS bead and the Pe molecules. We consider if the contribution of Pe to the total non-resonant refractive index is large compared with that of BPS bead, this mechanism will be a possible reason for the effective trapping due to the doping. In order to calculate the total non-resonant refractive index, we need to know these volume ratio. Since the volume of the BPS bead and the Pe molecule are, $\frac{4}{3}\pi r_{BP S}^3$ and $\frac{4}{3}\pi r_{Pe}^3$, respectively, the ratio is expressed as, $\frac{4}{3}\pi r_{Pe}^3 \times N$, where $r_{Pe}$, $r_{BPS}$ and $N$ are radius of the Pe molecule, that of BPS bead and number of the Pe in the BPS bead. The radius of the BPS bead $r_{BPS}$ and the Pe molecule $r_{Pe}$ are 21.5 nm and 4.7 Å that is estimated from the molar volume of the perylene. Therefore, for the sample of the PePS 230 and the PePS 457, from this expression, the ratios become about 0.24 % and 0.48 %, respectively. In the following, we show that these volume ratios have a very small contribution to the total non-resonant refractive index of PePS beads. On the other hand, in fact, the exact single Pe’s refractive index is not well known, therefore here we assume large refractive index as 10. In this matter, even if we assume the large refractive index, the influence to the total refractive index is very small. In particular, the polarizability is expressed as, $a = 4\pi r^3 \epsilon_0 \epsilon_2 \frac{m - \frac{1}{3}}{m + \frac{1}{3} + 2}$, where $m = \epsilon_1/\epsilon_2$ and $\epsilon_1$ and $\epsilon_2$ are dielectric constants of the molecule and surroundings, respectively (Here the effects of the radiation reaction is very small because the size of the particles are smaller than the wavelength of the trapping laser). Here, we estimate the polarizability ratio of BPS beads and Pe molecules, that is expressed as,

$$\frac{4\pi r_{Pe}^3 \epsilon_0 \epsilon_2 \frac{m_{Pe}}{m_{Pe} + 2} \times N}{4\pi r_{BPS}^3 \epsilon_0 \epsilon_2 \frac{m_{BPS}}{m_{BPS} + 2}}.$$  (7.1)

where $m_{Pe}$ and $m_{BPS}$ are $\epsilon_{Pe}/\epsilon_2$, $\epsilon_{BPS}/\epsilon_2$, respectively. ($\epsilon_{Pe} = 10$, $\epsilon_{BPS} = 1.57^2$ and $\epsilon_2 = 1.33^2$ for water). According to this equation, the ratio for the PePS 457 becomes about only 4 %. In other words, this means, by doping the Pe to the BPS bead, the absolute value of the polarizability is only changed about 4 %. This change is linearly proportional to the optical trapping potential, thus, it is too small to make a difference in the optical trapping behavior. As a conclusion in this section, we consider that this effect is not dominant in our experimental results.
7.5.2 Effect of aggregations on trapping

Here, in order to evaluate the effect of aggregation on trapping which we still found in the dynamic light scattering measurement (see the Section 7.3.1), we simply estimate and compare the number of the single particles and that of aggregated one, which will be drawn to the focal spot within a certain time.

In order to address to this matter, first, we calculate the concentrations and inter-particle distances of these particles. From the results of the dynamic light scattering (see the Fig.7.3), the percentages of the aggregations are about 2 % and 0.8 % for PePS 230 and PePS 457, respectively. Therefore, the concentrations of the aggregated PePS 230 and PePS 457 are $2.7 \times 10^{11}$ particles/ml and $1.08 \times 10^{11}$ particles/ml, respectively, estimating from the information of the single particles concentration ($1.35 \times 10^{13}$ particles/ml). Since 1 ml corresponds to 1 cm$^3$, the inter-particle distances of the aggregated PePS 230 and PePS 457 are about, $1 \mathrm{cm}/\sqrt{2.7 \times 10^{11}}=1.55 \mu\mathrm{m}$, and, $1 \mathrm{cm}/\sqrt{1.08 \times 10^{11}}=2.1 \mu\mathrm{m}$, respectively. The inter-particle distances of the single particles for both PePS 230 and PePS 457, are about $1 \mathrm{cm}/\sqrt{1.35 \times 10^{13}}=420 \mathrm{nm}$.

Next, we need to estimate the area in which the particles can be diffused to the focal spot, within a certain time by calculating the diffusion lengths. The diffusion distance, $R = \sqrt{\frac{2k_BT}{3\eta d^2}t}$ (where $k_B$, $T$, $\eta$, $d$ and $t$ are the Boltzmann constant, a temperature in Kelvin unit, 300 K, friction coefficient of the water, $0.89 \times 10^{-3}$ Pa s, diameter of the particles, and the irradiation time, respectively) of the single particles ($d = 43 \mathrm{nm}$) and aggregated one ($d = 120 \mathrm{nm}$) are $19 \mu\mathrm{m}$ and $11.1 \mu\mathrm{m}$ within $t = 15 \mathrm{s}$, respectively. Then, the volume of the area of single particles and aggregated one are, $4/3\pi(19\mu\mathrm{m})^3$ and $4/3\pi(11.1\mu\mathrm{m})^3$, respectively.

Finally, we know how many particles are inside the each volume area, by using the parameter of the inter-particles distances. Particularly, for the single particle, aggregated PePS 230 and aggregated PePS 457, the number of the particles inside the each volume area are about $3.88 \times 10^5$ particles, $1.54 \times 10^3$ particles and 620 particles, respectively.

Now, we know the maximum number of the particles that will be trapped at the focal spot. This maximum number means that all the particles come to the focal spot and are trapped at the focal spot. Under these assumptions, total volume of the trapped single particles, aggregated PePS 230, and aggregated PePS 457, are $1.62 \times 10^{-17}$ m$^3$, $1.39 \times 10^{-18}$ m$^3$, and $5.6 \times 10^{-19}$ m$^3$, respectively (the total volume will be linearly proportional to the scattering intensity). As we compare the single particles and the aggregated PePS 230, the total volume of the trapped single particles is more than ten times larger than the that of aggregated one. This indicates that the contribution of the aggregated particles to the scattering intensity is much weaker then that of the single particles. Actually, all the particles inside the volume area cannot diffuse to the focal spot because the particles will
diffuse for all directions, however these relation does not change even when we correctly estimate the number of the particles which diffuse to the focal spot by mean of the statistical mechanics. As a conclusion in this section, under these assumptions, aggregated particles does not affect the scattering intensity, that indicates in our experiment we are mainly observing the scattering intensity from the trapped “single” particles.

7.5.3 Effect of two-photon absorption

![Figure 7.8: Photon energy dependence of the radiation force along the direction of the focused beam. The Pe molecule is fixed at the $z = +300$ nm. Energy diagram for the assumed perylene is denoted in inset.](image)

Here, we investigate the two-photon resonance effect on the radiation force based on our theoretical calculation. To simply describe the idea, we only consider the radiation force exerted on the single perylene molecule. Energy diagram of the perylene is denoted in the inset of Fig. 7.8. The transition dipole moments $\mu_{21}$ and $\mu_{32}$, are 6 Debye and 0.3 Debye, respectively ($\mu_{32}$ is estimated from the experimentally measured two-photon absorption cross section of perylene, which is 54 GM at 800 nm [9]). The population decay times between 3-2 and 2-1 are 3 ps and 4 ns and that of 3-1 is neglected because this transition is one-photon forbidden. The dephasing constants are 0.2 meV. Perylene radius is assumed to be 4.7 Å and dielectric constant of the perylene is assumed to be 2.0.

With regard to the trapping laser, 800 nm CW laser is assumed in the calculation. According to the experimental condition, the laser power, NA and beam diameter before
the objective are 400 mW, 0.9, and 5 mm, respectively.

Figure 7.8 is the photon energy dependence of the radiation force along the direction of the focused beam. In this calculation, the Pe is located at the position $z = +300$ nm. As we see in Fig. 7.8, at the photon energy 1.515 eV that corresponds to the 800 nm in wavelength, there is a peak related to the two-photon resonance. However, the radiation force mainly act as the dissipative force that prevent trapping, namely, two-photon effects does not contribute to the optical trapping in this situation. In the present stage, the interpretation is under consideration, however, for the third order susceptibility, the imaginary part is larger than that of the real part. The imaginary part and the real part correspond to the dissipative force and the gradient force, respectively, therefore in this case, the dissipative force is larger than the gradient force, that is not suitable for the trapping condition.

On the other hand, there is a line curve which has a slop going down with increasing the photon energy. This is due to the tail of the one-photon resonance which is optically broadened with strong irradiation corresponding to optical saturation. Thus far, we have been considering that the two-photon resonance effects on the optical trapping, however there are one possibility that the tail of the one-photon resonance is responsible for the optical trapping. To investigate this point, we need to perform further experiment, for example, controlling the wavelength of the laser or changing the dopant dye molecule. We would like to discuss this issue in Section 7.6 for future works.

### 7.6 Conclusion and future works

We have subjected the optical trapping of the polystyrene nanoparticles doped by the perylene dye molecule that can be two-photon excited by using 800 nm CW laser. As a result, by individually measuring the scattering and the two-photon fluorescence intensities from the focal spot, we have found that, as a experimental fact, the dye doping effect makes the optical trapping more efficient than the case of non-doping. However the interpretation is still under investigation, therefore we suggest following future works, in order to completely reveal the phenomena underlying in this experiment.

**Dependence of perylene concentration in the polystyrene beads**

Perylene concentration in the present study was only twice different, therefore in order to clearly investigate the effect of the dye-doping, we need to expand the region of the Perylene concentration, for example 10 times or 100 times different Perylene concentrations. In the section of the result, we imply that higher Perylene concentration (PePS 457) is more effective than lower one (PePS 230), which will become clear by examining this experiment.
Dependence on laser wavelength and dopant of aromatic dye

In the discussion part (Section 7.5.3), we have raised the possibility of the tail of the one-photon excitation. To address this issue, changing the laser wavelength will be an appropriate way to investigate the effect of one-photon excitation. In particular, we can use the 1064 nm or 532 nm laser instead of 800 nm laser. When the detuning factor (difference between the laser wavelength and absorption wavelength of the dopant) is close to zero, the one-photon resonance becomes significant. Especially, when the laser wavelength is slightly longer than the absorption wavelength, the trapping becomes efficient. Also we can change the dopant which has other absorption energy levels, such as Rhodamine 6G, and so on.

Single particle detection

We can discuss the trapping behavior by using the scattering intensity and the two photon fluorescence intensity as we described in the present studies. However, those intensities are for an ensemble of the trapped nanoparticles. Therefore, in order to operate the accurate experiment, it is required to extend the experiment by using the single photon counter to detect the single particle trapping. By conducting this experiment, for example, trapping time can be measured experimentally that will be helpful to compare with the theoretical calculation. Also if we can obtain the distribution of the particle’s location, optical trapping potential is experimentally determined that will be also helpful for theoretical study.

Transient absorption spectroscopy

In order to experimentally investigate the resonant effect including the nonlinear optical effect, the transient absorption spectroscopy during the optical trapping will be a powerful tool.

We believe, dealing with these experiments, for the initial stage, we can elucidate the mechanism and maximize the ability of the dye-doping effect. Furthermore, utilizing fluorescence detection by means of the single photon counter and the transient absorption spectroscopy, nonlinear resonant optical manipulation will be experimentally confirmed with the aid of our theoretical studies.
References


Chapter 8

Summary and Outlook

8.1 Summary

We have proposed a theory of the radiation force involving the effect of nonlinear optical response that makes it possible to explain the paradoxes inherent in experiments of resonance optical tweezers for molecular trapping. This theory not only elucidates the puzzling discrepancies observed in experiments but also proposes an unconventional optical manipulation whose capability for manipulating nano-objects is highly enhanced due to the nonlinearity of optical response. In order to derive the nonlinear polarization for the calculation of the radiation force, we solve the motion equations of density matrix elements including the nonlinear optical effects beyond the perturbative regime. In the actual experiments, a very strong laser beam is focused on single molecules to provide sufficient radiation force for trapping, and therefore, it is necessary to take into account the nonlinearity of optical response beyond the perturbative regime.

As a consequence, in Chapter 3, the result with a simple two-level model indicates that the scattering force, which is a negative factor for molecular trapping, is suppressed as compared with the gradient force for trapping due to a strong saturation effect by the nonlinearity. Consequently, the trapping targets are not pushed away from the focal spot. On the other hand, in the case of blue-tuned trapping, the theory cannot explain the observed discrepancy only with the two-level model. However, if we consider the three-level energy scheme consisting of the vibrational levels typically existing in standard dye molecules, we can explain the trapping force by the laser with frequency above the resonance frequency (blue-tuned case), wherein the phase inversion of induced polarization due to inverted population is crucial to this effect. Further, if we utilize the mechanism of the nonlinear optical response, we can greatly improve the conventional trapping method by using two-color laser beams that enhance the trapping force by over one order of magnitude. As regards the case in which an assisting laser with considerably weaker
intensity than that of the main trapping laser aids in trapping, this can be explained by the mechanism of cascade excitations, wherein the nonlinear response also plays an essential role. These demonstrations to explain the experimental results indicate that resonance nonlinear optical manipulation has already been realized.

In Chapter 4, we have further proposed an unconventional optical manipulation method utilizing nonlinear optical response. The stimulated recoil force pulls the nanoparticles under the appropriate excitation condition for generating an inverted population. Thus, we can use this effect to sort particular kinds particles by controlling the beams for excitations. Subwavelength optical manipulation generates a small spot only where the strong force is induced, wherein the fact that the overlapped area of the two color beams is narrower than the light-wavelength is analogous to the principle underlying ultra-resolution optical microscopy. In Chapter 5, we have proposed the nonlinear resonant optical manipulation combined with the phenomena of the coherent transient process by using the resonant pulsed lasers. We have introduced the ideas of stimulated recoil force using π pulsed lasers and the radiation force that arises due to the interaction between polarization caused by the Rabi oscillation with the aid of the permanent dipole moment and the far infrared laser. In Chapter 6, moreover, we have theoretically demonstrated a radiation-induced interparticle force, which can aid in accelerating molecular trapping when the molecular density is high near the focal spot.

It should be remarked that our basic concept of resonant nonlinear optical manipulation can be applied also for the semiconductor nanoparticles and the metal nanoparticles though only the single organic molecules are treated in the present demonstrations. For semiconductor nanoparticles, considering the quantized electronic level schemes analogous to the molecules and their optical nonlinear properties, they are expected to be appropriate targets for experimental demonstration of our proposed effect. The metallic nanoparticles in some form might also be good targets to demonstrate the pulling force because the stimulated emission of surface plasmon polaritons is possible for hybrid nanoparticles consisting of metal core and surrounding dye doped silica shell [1].

Finally, in the Chapter 7, for experimental study, in order to investigate the resonant optical trapping that seems to be due to the nonlinear optical effect, we have conducted the experiment by ourself in Taiwan as a collaborative research. In particular, by individually measuring the scattering and the two-photon fluorescence intensities from the trapped particles at the focal spot we have found that, although the interpretation is still under consideration, as a experimental fact, the dye doping to polystyrene nanobeads makes the optical trapping more efficient than the case of non-doping even with the CW irradiation.
8.2 Outlook

As shown in this thesis, the theory of nonlinear resonant optical manipulation coherently elucidates some aspects of previous experimental results. However, considering all of these experimental reports were not aimed to investigate the nonlinear resonance optical effects on the optical trapping, we should say that the real advantage of optical manipulation utilizing nonlinear resonance optical effects has not been maximized yet. Thus, the experimental verification of the present idea is strongly desired.

Recently, in the collaborative experimental group (in National Chiao Tung University, Taiwan), they have reported the trapping of the nanoparticles by using the pulsed laser, that seems to be due to the two photon resonance which is one of the nonlinear resonance optical effect [2, 3] (this phenomenon cannot be observed by CW irradiation). We also have been conducting the related experiment in Taiwan by ourself and we have found that, even with the CW irradiation, the optical trapping becomes efficient due to the dye-doping to the nanoparticles, though the interpretation is still under consideration. Further, nonlinear optical effect on the optical trapping of gold nanoparticles has been experimentally observed by utilizing the femtosecond laser [4]. Although this result is not the case of resonance, also this evidence strongly supports the development of the nonlinear resonance optical trapping being based on our theoretical idea in future. If these nonlinear optical techniques can be used intentionally, as we proposed in this thesis, it might be possible to realize the trapping of single organic molecules, wherein sensitive control of the positioning of molecules can be realized. On the other hand, for the realization of such a technique, there are still several problems to be solved. One serious problem is that it is difficult to determine the absolute value of the induced force theoretically and experimentally. In particular, a discrepancy between the calculated force and the deduced one from experiments has been often observed [5]. In order to solve this problem, studies from both the theoretical and experimental sides are necessary to determine the unknown parameters of single molecules and analyze the detailed dynamics of biased molecules under laser illumination. We wish to emphasize that in such a study, the findings of the present study will play a central role in providing significant profiles of nanoparticle dynamics under intense laser illumination.

It should be remarked that in the recent experiments, a strong light field obtained with a femtosecond laser or a greatly magnified field obtained using localized plasmonic resonance is often applied [6–18]. Under such conditions, it is expected that the nonlinear process easily occurs. If the present nonlinear theory is applied to these experiments, more useful information could be obtained to develop a more powerful scheme of resonance optical manipulation. It is well-known that techniques of spectroscopy and photon manipulation in optical devices have shown explosive advances since the consideration
of nonlinear effects because nonlinear processes address a considerably larger number of degrees of freedom than the linear process. Similarly, we can expect that the intentional implementation of nonlinear processes in optical manipulation would greatly enhance the degrees of freedom to manipulate nano-objects.
References


Appendix A

Derivation of time-averaged radiation force

By taking the time-average of Eq. (2.1) and using the equations, \( H(r, \omega) = \nabla \times E(r, \omega)/i\omega \) and \( \frac{\partial P(r, \omega)}{\partial t} = -i\omega P(r, \omega) \), the equation for the time-averaged radiation force can be written as,

\[
\langle F(\omega) \rangle = \frac{1}{2} \text{Re} \left[ \int_V dr \{- (\nabla \cdot P(r, \omega)) E(r, \omega)^* + P(r, \omega) \times (\nabla \times E(r, \omega))^* \} \right]. \tag{A.1}
\]

Here, \( x \)-component of the first term in the integral can be expressed as follows by using the condition that the polarization at the object’s surface is zero (according to the boundary condition between outside and inside of the object, the amplitude of the polarization should be continuously changed, therefore, the polarization at the surface is zero),

\[
\left[ \int_V dr (\nabla \cdot P(r, \omega)) E(r, \omega)^* \right]_x = \int dx \int dy \int dz \left( \frac{\partial P_x}{\partial x} E_x^* + \frac{\partial P_y}{\partial y} E_y^* + \frac{\partial P_z}{\partial z} E_z^* \right)
\]

\[
= \int dy \int dz \left[ P_x E_x^* \right]_{x=\text{surface}} - \int dx \int dy \int dz P_x \left( \frac{\partial E_x^*}{\partial x} \right) \\
+ \int dx \int dz \left[ P_y E_y^* \right]_{y=\text{surface}} - \int dx \int dy \int dz P_y \left( \frac{\partial E_y^*}{\partial y} \right) \\
+ \int dx \int dy \left[ P_z E_z^* \right]_{z=\text{surface}} - \int dx \int dy \int dz P_z \left( \frac{\partial E_z^*}{\partial z} \right) \\
= - \int_V dr (P(r, \omega) \cdot \nabla) E_x(r, \omega)^*, \tag{A.2}
\]

and thus,

\[
- \int_V dr (\nabla \cdot P(r, \omega)) E(r, \omega)^* = \int_V dr (P(r, \omega) \cdot \nabla) E(r, \omega)^*. \tag{A.3}
\]
Next, the second term inside the integral of Eq. (A.1) can be expressed as,

$$\int \! d\mathbf{r} \mathbf{P}(\mathbf{r}, \omega) \times \nabla \times \mathbf{E}(\mathbf{r}, \omega)^* = \int \! d\mathbf{r} [(\nabla \mathbf{E}(\mathbf{r}, \omega)^*) \cdot \mathbf{P}(\mathbf{r}, \omega) - \mathbf{P}(\mathbf{r}, \omega) \cdot \nabla \mathbf{E}(\mathbf{r}, \omega)^*],$$

(A.4)

where, we use the identity,

$$\mathbf{a} \times \nabla \times \mathbf{c} = (\nabla \mathbf{c}) \cdot \mathbf{a} - (\mathbf{a} \cdot \nabla) \mathbf{c}. \quad \text{(A.5)}$$

Then, substituting Eq. (A.3) and (A.4) to Eq. (A.1), time averaged radiation force $\langle \mathbf{F}(\omega) \rangle$ can be written in a simple manner as [51, 54],

$$\langle \mathbf{F}(\omega) \rangle = (1/2) \text{Re} \int \! d\mathbf{r} [\nabla \mathbf{E}(\mathbf{r}, \omega)^*] \cdot \mathbf{P}(\mathbf{r}, \omega).$$
Appendix B

Expression for field gradient of tightly focused laser beam

To calculate the radiation force, we analytically derive the electric field gradient $\nabla E$ by using the following expressions that represent the gradients of $I_{00}$, $I_{01}$, and $I_{02}$,

$$\frac{dI_{00}}{dx} = -\int_0^\theta_{\text{max}} f_\omega(\theta) \sqrt{\cos\theta \sin\theta (1 + \cos\theta)}$$
$$\times \exp(ikz \cos\theta) \frac{kx}{\eta} \sin\theta J_1(k\eta \sin\theta) d\theta,$$

(B.1)

$$\frac{dI_{00}}{dy} = \int_0^\theta_{\text{max}} f_\omega(\theta) \sqrt{\cos\theta \sin\theta (1 + \cos\theta)}$$
$$\times \exp(ikz \cos\theta) \frac{ky}{\eta} \sin\theta J_1(k\eta \sin\theta) d\theta,$$

(B.2)

$$\frac{dI_{00}}{dz} = \int_0^\theta_{\text{max}} ik \cos\theta f_\omega(\theta) \sqrt{\cos\theta \sin\theta (1 + \cos\theta)}$$
$$\times J_0(k\eta \sin\theta) \exp(ikz \cos\theta) d\theta,$$

(B.3)

$$\frac{dI_{01}}{dx} = \frac{kx}{2\eta} \int_0^\theta_{\text{max}} f_\omega(\theta) \sqrt{\cos\theta \sin^2\theta \exp(ikz \cos\theta)}$$
$$\times \sin\theta (J_0(k\eta \sin\theta) - J_2(k\eta \sin\theta)) d\theta,$$

(B.4)

$$\frac{dI_{01}}{dy} = \frac{ky}{2\eta} \int_0^\theta_{\text{max}} f_\omega(\theta) \sqrt{\cos\theta \sin^2\theta \exp(ikz \cos\theta)}$$
$$\times \sin\theta (J_0(k\eta \sin\theta) - J_2(k\eta \sin\theta)) d\theta,$$

(B.5)
\[
\frac{dI_{01}}{dz} = \int_0^{\theta_{\text{max}}} ik \cos \theta f_\omega(\theta) \sqrt{\cos \theta \sin^2 \theta} \times J_1(k \eta \sin \theta) \exp(ikz \cos \theta) d\theta,
\]

\(\text{(B.6)}\)

\[
\frac{dI_{02}}{dx} = \frac{kx}{2 \eta} \int_0^{\theta_{\text{max}}} f_\omega(\theta) \sqrt{\cos \theta \sin \theta(1 - \cos \theta)} J_2(k \eta \sin \theta) \times \exp(ikz \cos \theta) \sin \theta(J_1(k \eta \sin \theta) - J_3(k \eta \sin \theta)) d\theta,
\]

\(\text{(B.7)}\)

\[
\frac{dI_{02}}{dy} = \frac{ky}{2 \eta} \int_0^{\theta_{\text{max}}} f_\omega(\theta) \sqrt{\cos \theta \sin \theta(1 - \cos \theta)} J_2(k \eta \sin \theta) \times \exp(ikz \cos \theta) \sin \theta(J_1(k \eta \sin \theta) - J_3(k \eta \sin \theta)) d\theta,
\]

\(\text{(B.8)}\)

\[
\frac{dI_{02}}{dz} = \int_0^{\theta_{\text{max}}} ik \cos \theta f_\omega(\theta) \sqrt{\cos \theta \sin \theta(1 - \cos \theta)} \times J_2(k \eta \sin \theta) \exp(ikz \cos \theta) d\theta.
\]

\(\text{(B.9)}\)
List of publications

Articles


Selected for the article


Invited paper

International conference presentations


5. T. Kudo and H. Ishihara, Resonant optical trapping utilizing nonlinear optical effects, SPIE is The International Society for optics and Photonice ”NanoScience + Engineering”(SPIE) (San Diego, USA, August, 2013), Poster.

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1. Tetsuhiro Kudo, Resonant optical manipulation based on nonlinear optical response, Award for Encouragement of Research in Condensed Matter Photophysics, granted by Association for Condensed Matter Photophysics, at Osaka City University, Japan, 10 December 2011.


Fellowships

1. Tetsuhiro Kudo, Research Fellowship for Young Scientists DC 2, granted by Japan Society for the Promotion of Science, April 2012 to March 2014.
2. Tetsuhiro Kudo, Postdoctoral Fellowship for Research Abroad, granted by Japan Society for the Promotion of Science, April 2014 to March 2016. (Expected)