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Comment

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# Comment on "Enantioselective Optical Trapping of Chiral Nanoparticles with Plasmonic Tweezers"

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We read with great interest the article "Enantioselective Optical Trapping of Chiral Nanoparticles with Plasmonic Tweezers" by Yang Zhao and collaborators, which appeared in ACS Photonics in 2016.[1] The authors expand the idea of chiral forces, which act differently on the enantiomers of a chiral substance, to propose an enantioselective optical trap. They theoretically analyzed such a trap based on a specifically designed plasmonic nanostructure and found that it traps only one enantiomer of a given chiral substance while repelling the other. Obviously, such a device would be highly interesting, especially for chemistry and pharmaceutics. However, we believe that there are severe difficulties for actual realizations of this effect, which we will discuss in this comment.

The total trapping force acting on the molecule is given as (cf. eq 3 in ref 1)

$$\mathbf{F}_{\mathrm{tr}} \approx \frac{\mathrm{Re}(\alpha_{\mathrm{ee}})}{4}\nabla|\mathbf{E}|^2 + \frac{\mathrm{Im}(\alpha_{\mathrm{em}})}{2}\nabla\mathrm{Im}(\mathbf{E}\cdot\mathbf{H}^*) \tag{1}$$

Here, $\alpha_{\mathrm{ee}}$ denotes the electric and $\alpha_{\mathrm{em}}$ the mixed electric-magnetic polarizability of the molecule. The latter connects the electric dipole moment to the magnetic field and, thus, gives rise to the chiral response; for the two enantiomers, its sign changes. Therefore, the trapping force can be decomposed in an achiral and a chiral part. The achiral contribution, which is proportional to the gradient of the electric energy density, is the same for both enantiomers; only the chiral component is handedness-dependent. For one enantiomer, the chiral component will lower the total trapping force; for the second, the total trapping force is increased.

A plasmonic optical trap is described by two parts, namely the plasmonic nanostructure that is used and the power of the illumination. This fixes both the electric energy density and the optical chirality density distributions. Such a trap will yield a certain achiral force. To be enantioselective, the additional chiral force must be strong enough that the resulting total force is above the trapping threshold for exactly one enantiomer. According to eq 1, this condition results in a lower limit for the ratio $\rho = \mathrm{Im}(\alpha_{\mathrm{em}})/\mathrm{Re}(\alpha_{\mathrm{ee}})$, which is specific for every individual trap.

In the work by Zhao et al., the chiral molecule has been modeled by a small sphere with an effective chiral medium described by the refractive index $n$ and the chirality parameter $\kappa$. Considering the above threshold for $\rho$, there will be a minimum $\kappa/n$ for which the trap acts enantioselectively. For the trap discussed in the article, this threshold is $\kappa/n = 0.14$. It is of major importance to note here that this value describes a substance with a considerably strong chiroptical response. Such values are in principle in reach for artificial chiral metamaterials, but exceed those of natural chiral molecules by orders of magnitude.[2] However, if artificial chiral molecules should be used, the validity of the approximations in the theory by Zhao et al. must be revisited. For example, many artificial chiral molecules are significantly larger in size than natural chiral molecules. Their size might conflict with the assumed quasi-static limit. As an additional consequence of the size, not all of the relevant resonances of the artificial chiral molecule will be located in the UV region, which was the precondition to neglect the vector forces. Furthermore, the strong electric dipole polarizability of artificial plasmonic molecules might lead to a substantial back-action of the chiral molecule onto the plasmonic trap. In this case, it would be necessary to numerically analyze the full system of the trap with the chiral molecule. As the chiral response of natural chiral substances is rather weak while artificial ones introduce additional challenges as sketched in this paragraph, we believe that it will be difficult to find a chiral substance suitable to demonstrate enantioselective trapping with the proposed design.

To address this issue, the authors suggested embedding the chiral molecule in an environment with matched permittivity. This seems to suppress $\alpha_{\mathrm{ee}}$ while maintaining $\alpha_{\mathrm{em}}$; i.e., it increases $\rho$ and, accordingly, the relative influence of the chiral trapping force. However, this finding is an artifact of the chosen model for the chiral molecule. If a given molecule should be modeled as a sphere made of an effective chiral medium, the effective parameters have to be chosen such that the resulting polarizabilities match those of the molecule in question. If such a sphere with fixed effective parameters is embedded in a different dielectric background, its properties change. For matching permittivities, the polarizability of the sphere vanishes. This is obvious as we now have a homogeneous permittivity and the only contribution to the electric dipole moment is due to the chirality of the sphere. However, a realistic molecule would not lose its electric polarizability just because it is embedded in a medium (see, for example, the calculations in ref 3). Therefore, the molecule would still react on the achiral gradient force. To model this behavior, one needs to adjust the effective parameters of the sphere as well, resulting in only minor changes to $\gamma$ and, accordingly, to $\kappa/n$.

Nevertheless, we believe that the general idea of enantioselective trapping is still viable. However, the trap should be designed specifically with this application in mind. We suggest the following scheme: First, the incident laser power should be tuned such that the achiral force exactly matches the trapping threshold. Then, any chiral contribution will theoretically trap one enantiomer (when the chiral force increases the total force) and repel the other (when the chiral force decreases the total force). In realistic scenarios, all these

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forces as well as the threshold will fluctuate (for example, due to intensity noise of the illumination laser or thermal fluctuations of the molecule). Therefore, *the chiral force must be stronger than all of these fluctuations combined*, which is a general condition for any scheme that utilizes chiral forces.[4] This can be supported by increasing the ratio between the chiral and the achiral force. Therefore, we suggest the explicit search for trap designs that optimize this ratio by increasing the optical chirality density gradient and lowering the electric energy density gradient.

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### Notes

The authors declare no competing financial interest.

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