

Laser optical separation of chiral molecules

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The optical trapping of molecules with an off-resonant laser beam involves a forward-Rayleigh scattering mechanism. It is shown that discriminatory effects arise on irradiating chiral molecules with circularly polarized light; the complete representation requires ensemble-weighted averaging to account for the influence of the trapping beam on the distribution of molecular orientations. Results of general application enable comparisons to be drawn between the results for two limits of the input laser intensity. It emerges that, in a racemic mixture, there is a differential driving force whose effect, at high laser intensities, is to produce differing local concentrations of the two enantiomers. © 2015 Optical Society of America

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The capacity of light to optically trap and manipulate microscopic, dielectric objects has been known since 1970 [1,2]. In this Letter, we show that the use of an optical trap with a single beam of circularly polarized light can provide a viable basis for separating chiral molecules of opposite handedness. At the nanoscale [3–6], optical trapping by an off-resonant laser beam can operate through a forward-Rayleigh scattering mechanism. Trapping of this type usually relates to the interaction of the laser field with a transition electric dipole, as shown by Fig. 1(a). Interactions between the irradiating beam and a transition magnetic dipole are also possible, but the associated coupling strength is usually much smaller in magnitude, and the effects are generally ignored. However, when considering the possibility of chiral discrimination (in which input light of left-handed circular polarization offers different observables compared to right-handed polarization), the conventional trapping mechanism involving only electric dipole transition moments has to be extended to accommodate transition magnetic dipoles [7]. In fact, the forward-Rayleigh scattering events most relevant in chiral discrimination involve a mixture of magnetic and electric dipole interactions, as illustrated by Fig. 1(b), with one kind of coupling involved in the input photon annihilation and the other in the output photon release.

To understand the energetics in greater detail, we note that the underlying mechanism for the optical trapping of molecules is based on the variation of intensity within the optical beam, which produces a position-dependent lowering of energy for the molecules it encounters: the alternating electric field of the radiation may be interpreted as producing a dynamic Stark shift to the molecular ground state energy. In terms of quantum electrodynamics, the energy shift (which is quadratically dependent on the electric field of the light) has to originate in forward-Rayleigh scattering, i.e., the concerted annihilation and creation of photons with identical energy and wave-vector. In such a case, the optical wavelengths will lie in a region of transparency for the irradiated molecule—the throughput laser beam therefore emerges unchanged. The primary physical determinant of optical trapping is the potential energy U , whose evaluation from quantum theory requires that the initial

and final states (here denoted by I) are identical [8]. An expression for U per molecule is determined from second-order time-dependent perturbation theory, i.e.,

$$U = \text{Re} \left\{ \sum_S \frac{\langle I | H_{\text{int}} | S \rangle \langle S | H_{\text{int}} | I \rangle}{E_I - E_S} \right\}, \quad (1)$$

where S is an intermediate state of the system comprising both molecule and radiation, E is the energy of the state denoted by its subscript, and H_{int} is the dipolar interaction Hamiltonian given by

$$H_{\text{int}} = -\boldsymbol{\mu} \cdot \mathbf{e} - \mathbf{m} \cdot \mathbf{b}. \quad (2)$$

Here, $\boldsymbol{\mu}$ and \mathbf{m} are the electric and magnetic dipole operators, respectively, while \mathbf{e} and \mathbf{b} are the electric and magnetic field operators, respectively. The latter may be cast in terms of photon number raising, a^\dagger , and lowering, a , operators—acting on radiation states $|n\rangle$ with n photons such that $a^\dagger|n\rangle = (n+1)^{1/2}|(n+1)\rangle$ and $a|n\rangle = n^{1/2}|(n-1)\rangle$. For present purposes the fields at position \mathbf{r} can be explicitly represented by

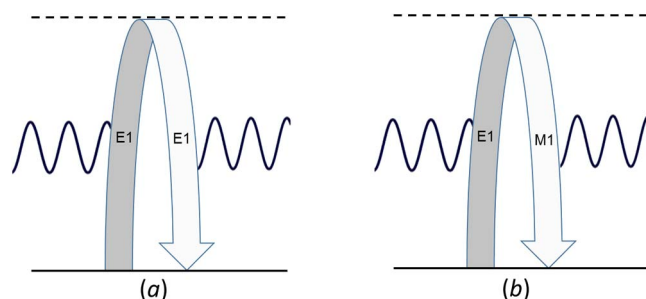


Fig. 1. Schematic energy level diagrams depicting forward-Rayleigh scattering that relate to (a) conventional optical trapping, involving two transition electric dipole (E1) interactions, and (b) optical separation of chiral molecules, comprising an electric and a magnetic dipole (M1) coupling (cases where E1 and M1 are interchanged are also included but not shown). Wavy line intercepts denote concerted absorption and emission due to the input laser beam, associated with upward and downward electronic transitions from the molecular ground state (horizontal solid line) to a virtual state (dotted line).

$$\mathbf{e}(\mathbf{r}) = i \left(\frac{I(\mathbf{r})}{2\epsilon_0 c} \right)^{\frac{1}{2}} \{ \mathbf{e}^{(L|R)} a e^{i(\mathbf{k}\cdot\mathbf{r})} - \bar{\mathbf{e}}^{(L|R)} a^\dagger e^{-i(\mathbf{k}\cdot\mathbf{r})} \}, \quad (3)$$

$$\mathbf{b}(\mathbf{r}) = i \left(\frac{I(\mathbf{r})}{2\epsilon_0 c^2} \right)^{\frac{1}{2}} \{ \mathbf{b}^{(L|R)} a e^{i(\mathbf{k}\cdot\mathbf{r})} - \bar{\mathbf{b}}^{(L|R)} a^\dagger e^{-i(\mathbf{k}\cdot\mathbf{r})} \}. \quad (4)$$

These expressions are cast in terms of the single radiation mode originating from the input laser—which is assumed to be circularly polarized with either a left-handed L or right-handed R polarization. Within Eqs. (3) and (4), $I(\mathbf{r})$ is the irradiance of the input beam at position \mathbf{r} , and $\mathbf{e}^{(L|R)}$ and $\mathbf{b}^{(L|R)}$ are the circular polarization vectors for the electric and magnetic fields, respectively, either left- or right-handed as denoted by the superscript.

Often the electric dipole approximation is applied in the theory of optical trapping, meaning that only the first term of Eq. (2) is considered—which corresponds to an electric dipole (E1) interaction. In most cases this approximation is valid, but in studies on chirality the magnetic dipole M1 interactions must also be employed. Since optical binding calculations involve two interactions, explaining the two appearances of H_{int} in Eq. (1), both electric dipole-electric dipole (E1²) and electric dipole-magnetic dipole (E1M1) interactions are utilized. On input of a circularly polarized beam of either specific handedness, the optical trapping potential of a chiral molecule is determined, using Eqs. (1) and (2) as the starting point, as follows:

$$U^{(L|R)}(\mathbf{r}) = - \left(\frac{I(\mathbf{r})}{2\epsilon_0 c^2} \right) \text{Re} \{ c \bar{e}_i^{(L|R)} e_j^{(L|R)} \alpha_{ij} + \bar{e}_i^{(L|R)} b_j^{(L|R)} G_{ij} + \bar{b}_i^{(L|R)} e_j^{(L|R)} \tilde{G}_{ji} + \dots \}, \quad (5)$$

in which α_{ij} is the polarizability tensor, constructed in the usual way from weighted products of transition electric dipole components, and G_{ij} is a counterpart electric-magnetic dipolar scattering tensor, which has a standard definition [9]; a summation over repeated Cartesian indices i, j is implied. The directionality of the optical force, corresponding to $U^{(L|R)}(\mathbf{r})$, is determined from the intensity profile of the beam as follows from $I(\mathbf{r})$. In a cylindrically symmetric beam, the optical trapping (gradient) force acts radially with respect to the high intensity regions of the beam, with a sign determined by a positive or negative detuning from resonance: for Gaussian light the beam intensity is highest at the center, but in many forms of structured or ‘donut beam’ light, the intensity at the beam center is zero.

Our main focus, in the following, is the leading nonzero term with a capacity for chiral discrimination—this, as will be shown, corresponds to the E1M1 interaction. A quantitative analysis of optical discrimination involves determination of the difference between the potential energy associated with the scattering of left-handed circularly polarized light compared to a right-handed polarization, as denoted by $U^{(L-R)} \equiv U^{(L)} - U^{(R)}$. It is significant that the same discriminatory results arise when light of a single circular polarization impinges upon chiral molecules of left-handed relative to right-handed form, which in this case signifies a capacity for the separation

of such molecules. The additional, distinctive optical force contribution that arises in cases of molecular chirality is expressible as $\mathbf{F}^{(L|R)}(\mathbf{r}) = -\nabla(U^{(L|R)}(\mathbf{r}))$, leading to a differential force, $\Delta\mathbf{F}(\mathbf{r}) \equiv \mathbf{F}^{(L)}(\mathbf{r}) - \mathbf{F}^{(R)}(\mathbf{r})$, that quantifies a propensity for enantiomer separation—the means are to be discussed later. The broad context of optical methods for chiral discrimination is indeed a subject of considerable current interest [10–17]. An expression for such discrimination is determined from Eq. (5) as

$$U^{(L-R)}(\mathbf{r}) = i \left(\frac{I(\mathbf{r})}{2\epsilon_0 c^2} \right) (\bar{e}_i^{(L)} e_j^{(L)} + \bar{e}_i^{(R)} e_j^{(R)}) (G_{ij} - \tilde{G}_{ji}), \quad (6)$$

in which the E1² (polarizability) term cancels out, and the identity $b_i^{(L|R)} = \mp i e_i^{(L|R)}$ is employed. We note that G_{ij} and \tilde{G}_{ji} are imaginary quantities, each of equal magnitude but opposite sign for the two enantiomers. In consequence, the corresponding differential force $\Delta\mathbf{F}(\mathbf{r})$, determined by the local intensity distribution, has a sign that may differ from the net force $\mathbf{F}^{(L|R)}(\mathbf{r})$, according to the handedness of the enantiomer. The above expression may be recast as

$$U^{(L-R)}(\mathbf{r}) = - \left(\frac{I(\mathbf{r})}{\epsilon_0 c^2} \right) (\delta_{ij} - \hat{k}_i \hat{k}_j) G'_{ij}, \quad (7)$$

by using a further identity $\bar{e}_i^{(L)} e_j^{(L)} + \bar{e}_i^{(R)} e_j^{(R)} = \delta_{ij} - \hat{k}_i \hat{k}_j$ and setting $\text{Im} G_{ij} \equiv G'_{ij}$. We note that the chiral force, dependent on $\nabla I(\mathbf{r})$, is thus proportional to all the other factors in Eq. (7). For conciseness in the following development, the \mathbf{r} dependence in explicit equations is suppressed.

Up until this point, it has been assumed that the molecules are set in a fixed position. Our next step is the determination of physical effects due to the dynamic interaction of the molecules with the optical trapping beam; this contrasts with a model of freely tumbling molecules. Achieving such an aim requires a three-dimensional ensemble average (i.e., through $-\alpha\mathcal{E}^2$, where \mathcal{E} is the electric field deriving from the input beam) reflecting the fact that trapped chiral molecules experience a partial orientation effect, compromised by thermal fluctuations. As a result of this anisotropic interaction with the laser beam, the mean potential energy of the trapping interaction is subject to a weighted orientational distribution. To analytically evaluate the potential energy with the appropriately weighted averages introduces some demanding mathematics: a complete theoretical representation has only recently become possible [18], finding its first application in connection with optical binding [19]. The initial step is represented by the following;

$$\langle U^{(L-R)} \rangle \equiv - \left(\frac{I}{\epsilon_0 c^2} \right) \frac{\langle \mathbf{A} \cdot \mathbf{B} \exp(\mathbf{C} \cdot \mathbf{D}) \rangle}{\langle \exp(\mathbf{C} \cdot \mathbf{D}) \rangle}, \quad (8)$$

where \mathbf{A} , \mathbf{B} , \mathbf{C} and \mathbf{D} are rank-2 tensors, the colons represent an inner product between two such tensors, and the chevrons denote an ensemble average. The form of this result might be compared, for example, with a much simpler case involving only a rank-1 (vector) form of coupling, as in the Langevin formula for the mean dipole in a static field, for example [20]. In the present

case, **A** and **C** refer to the optical stimuli, which are considered in the laboratory frame of reference, and **B** and **D** correspond to the molecular response that is fixed by reference to its own (molecular) frame. Using Eq. (7) and a weighting factor $-\alpha\mathcal{E}^2$, it is clear that the necessary result can be evaluated by the substitutions $\mathbf{A} = G'_{ij}$, $\mathbf{B} = \delta_{ij} - \hat{k}_i\hat{k}_j$, $\mathbf{C} = \beta\alpha_{ij}$ ($\beta = \mathcal{E}^2/k_B T$, where the denominator is a product of the Boltzmann constant and temperature) and $\mathbf{D} = \frac{1}{2}(\delta_{ij} - \hat{k}_i\hat{k}_j)$.

It is now expedient to introduce an irreducible tensor decomposition, in which the rank-2 tensors are written in terms of a summation of their weightings so that $\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(1)} + \mathbf{A}^{(2)}$, for example, where the superscripts denote the weight and $\mathbf{A}^{(0)}$ transforms as a scalar, $\mathbf{A}^{(1)}$ as a vector and $\mathbf{A}^{(2)}$ as a symmetric, traceless second rank tensor [21]. By use of the latter, an explicit form of Eq. (8) may be written, i.e.:

$$\langle U^{(L-R)} \rangle = -\left(\frac{I}{\epsilon_0 c^2}\right) \left\{ \langle \mathbf{A}^{(0)} \cdot \mathbf{B}^{(0)} \rangle + \left[\sum_{m=0}^3 \frac{1}{m!} \langle (\mathbf{A}^{(2)} \cdot \mathbf{B}^{(2)}) (\mathbf{C}^{(2)} \cdot \mathbf{D}^{(2)})^m \rangle \right] // \left[\sum_{m=1}^4 \frac{1}{m!} \langle (\mathbf{C}^{(2)} \cdot \mathbf{D}^{(2)})^m \rangle \right] \right\}. \quad (9)$$

Here, $\mathbf{A}^{(0)} = \frac{1}{3}\delta_{ij}G'_{\lambda\lambda}$, $\mathbf{B}^{(0)} = 2\mathbf{D}^{(0)} = \frac{2}{3}\delta_{ij}$, $\mathbf{C}^{(0)} = \frac{1}{3}\beta\delta_{ij}\alpha_{\lambda\lambda}$, $\mathbf{A}^{(2)} = \frac{1}{2}(G'_{ij} + G'_{ji}) - \frac{1}{3}\delta_{ij}G'_{\lambda\lambda}$, $\mathbf{C}^{(2)} = \beta(\alpha_{ij} - \frac{1}{3}\delta_{ij}\alpha_{\lambda\lambda})$, $\mathbf{B}^{(2)} = \frac{1}{3}\delta_{ij} - \hat{k}_i\hat{k}_j$, and $\mathbf{D}^{(2)} = \frac{1}{2}(\frac{1}{3}\delta_{ij} - \hat{k}_i\hat{k}_j)$. (In the present case, the second term of Eq. (4.2) in ref. [18] is omitted since $\mathbf{B}^{(1)} = 0$ and, additionally, $n = m$ since $\mathbf{C}^{(1)} = 0$.) On application of the relevant rank of rotational average [22,23] for each term in Eq. (9), the following result is found:

$$\langle U^{(L-R)} \rangle = -\left(\frac{I}{\epsilon_0 c^2}\right) \left\{ 2G + 2\beta[G^\alpha - G\alpha - \frac{\beta}{21}(G^{aaa} + 3G \times (2\alpha^2 - \alpha^\alpha) - 6G^\alpha\alpha) + \frac{\beta^2}{1450}(3G^\alpha(13\alpha^\alpha - 3\alpha^2) + 9G\alpha \times (\alpha^2 - \alpha^\alpha) + 10(G^{aaaa} - 3G^{aaa}\alpha - 2G\alpha^{aaa}))] \times \left(10 + \beta^2 \left[\alpha^\alpha - \alpha^2 - \frac{\beta}{21}(\alpha^{aaa} + \alpha(2\alpha^2 - 3\alpha^\alpha)) \right] + \frac{\beta^2}{58000}(3\alpha^\alpha(13\alpha^\alpha - 6\alpha^2) + 10\alpha^{aaaa} - 40\alpha^{aaa}\alpha + 9\alpha^4) \right]^{-1} \right\}, \quad (10)$$

with a simplified notation $\alpha = \frac{1}{3}\alpha_{\lambda\lambda}$, $\alpha^\alpha = \frac{1}{3}\alpha_{\lambda\mu}\alpha_{\lambda\mu}$, $G^\alpha = \frac{1}{3}G'_{\lambda\mu}\alpha_{\lambda\mu}$, $G^{aaa} = \frac{1}{6}(G'_{\lambda\mu}\alpha_{\mu\nu}\alpha_{\nu\lambda} + G'_{\mu\lambda}\alpha_{\mu\nu}\alpha_{\nu\lambda})$, $G = \frac{1}{3}G'_{\lambda\lambda}$, $G^{aaaa} = \frac{1}{6}(G'_{\lambda\mu}\alpha_{\mu\nu}\alpha_{\nu\sigma}\alpha_{\sigma\lambda} + G'_{\mu\lambda}\alpha_{\mu\nu}\alpha_{\nu\sigma}\alpha_{\sigma\lambda})$, $\alpha^{aaa} = \frac{1}{3}\alpha_{\lambda\mu}\alpha_{\mu\nu}\alpha_{\nu\sigma}\alpha_{\sigma\lambda}$, $\alpha^{aaa} = \frac{1}{3}\alpha_{\lambda\mu}\alpha_{\mu\nu}\alpha_{\nu\lambda}$. From this general result, it emerges that at one extreme, when the electric field of the input beam is very small, i.e., $\beta \rightarrow 0$, the isotropic result of $\langle U^{(L-R)} \rangle = -2GI/\epsilon_0 c^2$ is obtained, in agreement with previous work [7]. In contrast, at the other extreme where \mathcal{E} is very

large—namely, cases with strong orientation effects—the following expression is found from Eq. (10):

$$\langle U^{(L-R)} \rangle = -\left(\frac{80I}{\epsilon_0 c^2}\right) \{ 3G^\alpha(13\alpha^\alpha - 3\alpha^2) + 9G\alpha(\alpha^2 - \alpha^\alpha) + 10(G^{aaaa} - 3G^{aaa}\alpha - 2G\alpha^{aaa}) \} (3\alpha^\alpha(13\alpha^\alpha - 6\alpha^2) + 10\alpha^{aaaa} - 40\alpha^{aaa}\alpha + 9\alpha^4)^{-1}, \quad (11)$$

which is determined from the terms associated with the highest order of β in the numerator and denominator.

It proves highly informative to take one special case of Eq. (11) to achieve three separate objectives: one is to verify the correct form of the expression; second, to identify a lower bound for typical magnitudes of the effect, and third, to secure a result for a specific potential application. To this end, the condition we now apply is an approximation based on the physical case of a molecule that is essentially isotropic, yet chiral. (The study of notionally chiral spheres is a subject that has itself attracted recent interest [24–27].) Applying this assumption means that we can write $G = g$, $\alpha = a$, $G^\alpha = 3ag$, $\alpha^\alpha = 3a^2$, $G^{aaa} = 9a^2g$, $\alpha^{aaa} = 9a^3$, $G^{aaaa} = 27a^3g$, $\alpha^{aaaa} = 27a^4$, where a and g are isotropic electric-electric and electric-magnetic scattering scalars, respectively. By insertion of these factors into Eq. (11), the following greatly simplified expression is obtained:

$$\langle U^{(L-R)} \rangle = -\left(\frac{140I}{3\epsilon_0 c^2}\right) \left(\frac{g}{\beta a}\right). \quad (12)$$

This result shows that the corresponding differential force is smaller than the dominant ($E1^2$) force by a factor of $70g/3ac$. Since it can be anticipated that the values of the elements of the **G** tensor, divided by c , will in general be smaller than those of the polarizability by a factor of approximately 137, the inverse of the fine structure constant, this means that the differential $E1M1$ effect is roughly 1/6 that of the $E1^2$ leading term. Taking one enantiomer, the total force thus acquires contributions from the $E1^2$ and $E1M1$ interactions (the latter being 1/12 the magnitude of the former). For its stereoisomer, the $E1M1$ interactions are necessarily of opposite sign, and hence, the net force it experiences is smaller. Therefore, the difference in the optical force trapping between the two enantiomers is $F_0/6$, where F_0 is the optical force due to the $E1^2$ interaction. For example, at room temperature, a molecule with a polarizability volume ($\alpha/4\pi\epsilon_0$) of 10^{-29} m^3 , in a beam of focused intensity $5 \times 10^{11} \text{ W cm}^{-2}$ and beam waist $10 \text{ }\mu\text{m}$, should experience differential forces of 10^{-16} N or more—considered well within experimental reach [13]. It is interesting that any real chiral molecule is likely to have significantly different values for its individual polarizability components (so too, the **G** tensor), since these types of molecules are typically far from isotropic. In consequence, one can suppose that the examined case represents a likely lower bound for the extent of chiral separation achievable in real systems when \mathcal{E} is large.

In conclusion, we have detailed a mechanism to separate left- and right-handed chiral molecules. While, as expected, the difference in the optical force for the

two enantiomers is small, our results suggest that the laser-induced chiral force is significant, experimentally measurable, and, as shown by the model calculations, potentially sizeable at high levels of laser intensity. The physical significance of the result, relating to a continuously irradiated racemic mixture of the two enantiomers, is a minimized system energy with one enantiomer selectively driven more than the other toward a local intensity maximum (or minimum), thus producing a difference in the time-averaged concentrations of the two enantiomers. Our results make no assumption about the spatial form of the intensity distribution, which need not be limited to beams with constant circular polarization, nor intensity distributions of radial symmetry and simple Gaussian cross-section. It is clear that locally different forces will arise according to the specific beam structure; examples of more intricate behavior may be afforded by vector beams with transverse variations in polarization [28–30], which are the subject of ongoing analysis. It is indeed anticipated that beams with spatially varying polarization may enhance the effect of enantiomer separation, especially since such beams are known to engender unusual forces and torques [31]. As such, the proposed system has numerous advantages over several previous proposals, for example, the microwave spectroscopy method [15] detects but does not separate the enantiomers and only applies to the gas phase, which is unsuitable for large chiral molecules. Advantages compared to a two-step switch [10,11] arise from the fact that no excitation is required, resulting in a less energetic system with no time delays due to molecular recovery. The mechanism we have described therefore appears a promising candidate for experimental investigation, with a view to its possible implementation for enantiomer separation.

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References

1. A. Ashkin, Phys. Rev. Lett. **24**, 156 (1970).
2. A. Ashkin, IEEE J. Selected Top. Quant. Electr. **6**, 841 (2000).
3. M. Dienerowitz, M. Mazilu, and K. Dholakia, J. Nanophoton. **2**, 021875 (2008).
4. T. Čížmár, L. C. Dávila Romero, K. Dholakia, and D. L. Andrews, J. Phys. B: At. Mol. Opt. Phys. **43**, 102001 (2010).
5. O. M. Marago, P. H. Jones, P. G. Gucciardi, G. Volpe, and A. C. Ferrari, Nat. Nanotechnol. **8**, 807 (2013).
6. R. W. Bowman and M. J. Padgett, Rep. Prog. Phys. **76**, 026401 (2013).
7. D. S. Bradshaw and D. L. Andrews, New J. Phys. **16**, 103021 (2014).
8. D. S. Bradshaw and D. L. Andrews, J. Phys. Chem. A **117**, 75 (2013).
9. D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics: An Introduction to Radiation-Molecule Interactions* (Dover, 1998).
10. P. Král, I. Thanopoulos, M. Shapiro, and D. Cohen, Phys. Rev. Lett. **90**, 033001 (2003).
11. W. Z. Jia and L. F. Wei, J. Phys. B **43**, 185402 (2010).
12. X. Li and M. Shapiro, J. Chem. Phys. **132**, 194315 (2010).
13. A. Canaguier-Durand, J. A. Hutchison, C. Genet, and T. W. Ebbesen, New J. Phys. **15**, 123037 (2013).
14. A. Eilam and M. Shapiro, Phys. Rev. Lett. **110**, 213004 (2013).
15. D. Patterson, M. Schnell, and J. M. Doyle, Nature **497**, 475 (2013).
16. R. P. Cameron, S. M. Barnett, and A. M. Yao, New J. Phys. **16**, 013020 (2014).
17. R. P. Cameron, A. M. Yao, and S. M. Barnett, J. Phys. Chem. A **118**, 3472 (2014).
18. S. N. A. Smith and D. L. Andrews, J. Phys. A **44**, 395001 (2011).
19. S. N. A. Smith, M. M. Coles, and D. L. Andrews, Proc. SPIE **8097**, 80971E (2011).
20. C. E. Hecht, *Statistical Thermodynamics and Kinetic Theory* (W. H. Freeman, 1990).
21. D. L. Andrews and P. Allcock, *Optical Harmonics in Molecular Systems* (Wiley-VCH, 2002).
22. D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **67**, 5026 (1977).
23. D. L. Andrews and W. A. Ghoul, J. Phys. A **14**, 1281 (1981).
24. D. V. Guzatov and V. V. Klimov, New J. Phys. **14**, 123009 (2012).
25. Z.-S. Wu, Q.-C. Shang, and Z.-J. Li, Appl. Opt. **51**, 6661 (2012).
26. Q.-C. Shang, Z.-S. Wu, T. Qu, Z.-J. Li, L. Bai, and L. Gong, Opt. Express **21**, 21879 (2013).
27. V. V. Klimov, I. V. Zabkov, A. A. Pavlov, and D. V. Guzatov, Opt. Express **22**, 18564 (2014).
28. Q. Zhan, Adv. Opt. Photon. **1**, 1 (2009).
29. G. Milione, H. I. Sztul, D. A. Nolan, and R. R. Alfano, Phys. Rev. Lett. **107**, 053601 (2011).
30. G. M. Philip, V. Kumar, G. Milione, and N. K. Viswanathan, Opt. Lett. **37**, 2667 (2012).
31. D. B. Ruffner and D. G. Grier, Phys. Rev. Lett. **108**, 173602 (2012).