Deflection of field-free aligned molecules

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We consider deflection of polarizable molecules by inhomogeneous optical fields, and analyze the role of molecular orientation and rotation in the scattering process. It is shown that molecular rotation induces spectacular rainbow-like features in the distribution of the scattering angle. Moreover, by pre-shaping molecular angular distribution with the help of short and strong femtosecond laser pulses, one may efficiently control the scattering process, manipulate the average deflection angle and its distribution, and reduce substantially the angular dispersion of the deflected molecules. This opens new ways for many applications involving molecular focusing, guiding and trapping by optical and static fields.

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Optical deflection of molecules by means of nonresonant laser fields is a hot subject of many recent experimental studies References. By controlling molecular translational degrees of freedom References, novel elements of molecular optics can be realized, including molecular lens References and molecular prism References. The mechanism of molecular deflection by a nonuniform laser field is rather clear: the field induces molecular polarization, interacts with it, and deflects the molecules along the intensity gradient. As most molecules have anisotropic polarizability, the deflecting force depends on the molecular orientation with respect to the deflecting field. Previous studies on optical molecular deflection have mostly considered randomly oriented molecules, for which the deflection angle is somehow dispersed around the mean value determined by the orientation-averaged polarizability. The latter becomes intensity-dependent for strong enough fields due to the field-induced modification of the molecular angular motion References, References. This adds a new ingredient for controlling molecular trajectories References, References, which is important, but somehow limited because of using the same fields for the deflection process and orientation control.

In this Letter, we show that the deflection process can be significantly affected and controlled by pre-shaping molecular angular distribution before the molecules enter the interaction zone. This can be done with the help of numerous recent techniques for laser molecular alignment, which use single or multiple short laser pulses (transform-limited, or shaped) to align molecular axes along certain directions. Short laser pulses excite rotational wavepackets, which results in a considerable transient molecular alignment after the laser pulse is over, i.e. at field-free conditions (for recent reviews on field-free alignment, see, e.g. References, References). Field-free alignment was observed both for small diatomic molecules as well as for more complex molecules, for which full three-dimensional control was realized References, References, References, References, References. We demonstrate that the average scattering angle of deflected molecules and its distribution may be dramatically modified by a proper field-free pre-alignment. By separating the processes of the angular shaping and actual deflection, one gets a flexible tool for tailoring molecular motion in inhomogeneous optical and static fields.

Although our arguments are rather general, we follow for certainty a deflection scheme that reminds the experiment by Stapelfeldt et al References who used a strong IR laser to deflect a CS$_2$ molecular beam, and then addressed a portion of the deflected molecules (at a preselected place and time) by an additional short and narrow ionizing pulse. Consider deflection (in z direction) of a linear molecule moving in x direction with velocity $v_x$ and interacting with a focused nonresonant laser beam that propagates along the y axis. The spatial profile of the laser electric field in the xz-plane is $E = E_0 \exp[-(x^2 + z^2)/\omega_0^2] \exp[-2 \ln 2 t^2/\tau^2]$. The interaction potential of a linear molecule in the laser field is given by:

$$U(t) = -\frac{1}{4}E^2 (\alpha_|| \cos^2 \theta + \alpha_\perp \sin^2 \theta),$$

where $E$ is defined above, and $\alpha_||$ and $\alpha_\perp$ are the components of the molecular polarizability along the molecular axis, and perpendicular to it, respectively. Here $\theta$ is the angle between the electric field polarization direction (along the laboratory z axis) and the molecular axis. A molecule initially moving along the x direction will acquire a velocity component $v_z$ along z-direction. We consider the perturbation regime (weak field approximation) corresponding to a small deflection angle, $\gamma \approx v_z/v_x$. We substitute $x = v_x t$, and consider $z$ as a fixed impact parameter. The deflection velocity is given by:

$$v_z = \frac{1}{M} \int_{-\infty}^{\infty} F_z(t) dt = -\frac{1}{M} \int_{-\infty}^{\infty} \left( \nabla U(t) \right)_z, \quad (2)$$

Here $M$ is the mass of the molecules, and $F_z$ is the deflecting force. The time-dependence of the force $F_z(t)$ (and potential $U(t)$) in Eq (2) comes from three sources: pulse envelope, projectile motion of the molecule through the laser focal area, and time variation of the angle $\theta$ due to molecular rotation. For simplicity, we assume that the deflecting field does not affect significantly the rotational motion. Such approximation is justified, say for CS$_2$ molecules with the rotational temperature $T = 5K$, which are subject to the deflecting field of...
3 \times 10^3 \text{W/cm}^2. \) The corresponding alignment potential \( U \approx -\frac{1}{4}(\alpha_0 - \alpha_\perp)E_0^2 \approx 0.04 \text{ meV} \) is an order of magnitude smaller than the thermal energy \( k_B T \), where \( k_B \) is Boltzmann’s constant. This assumption is even more valid if the molecules were additionally subject to the aligning pulses prior to deflection.

Since the rotational time scale is the shortest one in the problem, we average the force over the fast rotation, and arrive at the following expression for the deflection angle, \( \gamma = v_z/v_x \):

\[
\gamma = \gamma_0 \left( \frac{\alpha_\parallel A + \alpha_\perp (1 - A)}{\alpha_0} \right) / \overline{\alpha}
\]  

(3)

Here \( \overline{\alpha} = 1/3\alpha_\parallel + 2/3\alpha_\perp \) is the orientation-averaged molecular polarizability, and \( A = \cos^2 \theta \) denotes the time-averaged value of \( \cos^2 \theta \). This quantity depends on the relative orientation of the vector of angular momentum and the polarization of the deflecting field. It is different for different molecules of the incident ensemble, which process the constant \( \gamma_0 \) presents the average deflection angle for an isotropic molecular ensemble:

\[
\gamma_0 = \frac{\pi E_0^2}{4M v_x^2} \left( -\frac{4z}{\omega_0} \right) \times \sqrt{\frac{\pi}{2}} \left( 1 + \frac{2\omega_0^2 \ln 2}{\pi^2 v_x^2} \right)^{-1/2} \exp \left( -\frac{2x^2}{\omega_0^2} \right)
\]  

(4)

We provide below some heuristic classical arguments on the anticipated statistical properties of \( A \) and \( \gamma \) (both for thermal and pre-aligned molecules) and then support them by a more refined quantum treatment.

Consider a linear molecule that rotates freely in a plane that is perpendicular to the vector \( \vec{J} \) of the angular momentum (see Fig. 1).

\[\begin{align*}
\text{FIG. 1: A molecule rotates with a given angular momentum } &\vec{J} \text{ that is randomly oriented in space. } \\
\text{angular momentum is } &\theta_J \text{ the angle between the angular momentum and the laboratory } z \text{ axis.}
\end{align*}\]

The projection of the molecular axis on the vertical \( z \)-direction is given by \( \cos \theta(t) = \cos(\omega t) \sin \theta_J \), where \( \theta_J \) is the angle between \( \vec{J} \) and \( z \)-axis, and \( \omega \) is the angular frequency of molecular rotation. Averaging over time, one arrives at:

\[
A = \cos^2 \theta = \frac{1}{2} \sin^2 \theta_J.
\]  

(5)

In a thermal ensemble, vector \( \vec{J} \) is randomly oriented in space, with isotropic angular distribution \( 1/2 \sin(\theta_J) d\theta_J \). The mean value of the deflection angle is \( \langle \gamma \rangle = \gamma_0 \). Eq. (5) allows us to obtain the distribution function, \( f(A) \) for \( A \) (and the related deflection angle) from the known isotropic distribution for \( \theta_J \). Since the inverse function \( \theta_J(A) \) is multivalued, one obtains

\[
f(A) = \frac{2}{\pi} \frac{1}{\sqrt{A(1 - 2A)}}
\]  

(6)

where we summed over the two branches of \( \theta_J(A) \). This formula predicts an unimodal rainbow singularity in the distribution of the scattering angles at the maximal value \( \gamma = \gamma_0(\alpha_\parallel + \alpha_\perp)/2\alpha \) (for \( A = 1/2 \)), and a flat step near the minimal one \( \gamma = \gamma_0\alpha_\perp/\alpha_\perp \) (for \( A = 0 \)). Assume now that the molecules are pre-aligned before entering the deflection zone by a strong and short laser pulse that is polarized perpendicular to the polarization direction of the deflecting field (e.g., in \( z \)-direction). Such a pulse forces the molecules to rotate preferentially in the planes containing the \( x \)-axis. As a result, the vector \( \vec{J} \) of the angular momentum is confined to the \( yz \)-plane, and angle \( \theta_J \) becomes uniformly distributed in the interval \([0, \pi]\) with probability density \( d\theta_J/\pi \). The corresponding probability distribution for \( A \) takes the form

\[
f(A) = \frac{\sqrt{2}}{\pi} \frac{1}{\sqrt{A(1 - 2A)}}
\]  

(7)

In contrast to Eq. (6), formula Eq. (7) suggests a bimodal rainbow in the distribution of deflection angles, with singularities both at the minimal and the maximal angles. Finally, we proceed to the most interesting case when the molecules are pre-aligned by a short strong laser pulse that is polarized parallel to the direction of the deflecting field. After excitation by such a pulse, the vector of the angular momentum of the molecules is preferentially confined to the \( xy \)-plane, and angle \( \theta_J \) takes a well-defined value of \( \theta_J \approx \pi/2 \). As a result, the dispersion of the scattering angles is reduced dramatically. The distribution of the deflection angle \( \gamma \) transforms to a narrow peak (asymptotically - a \( \delta \)-function) near the maximal value, \( \gamma = \gamma_0(\alpha_\parallel + \alpha_\perp)/2\alpha \).

For a more quantitative treatment, involving analysis of the relative role of the quantum and thermal effects on one hand, and the strength of the pre-aligning pulses on the other hand, we consider quantum-mechanically the deflection of a linear molecule described by the Hamiltonian \( H = J^2/(2I) \). Here \( J \) is operator of angular momentum, and \( I \) is the moment of inertia, which is related to the molecular rotational constant, \( B = h/(4\pi Ic) \) (\( c \) is speed of light). Assuming again that the deflecting field is too weak to modify molecular alignment, we consider scattering in different \( J, m \) states independently. The deflection angle is given by Eq. (5), in which \( A \) is replaced by

\[
A_{J,m} = \langle J, m | \cos^2 \theta | J, m \rangle = \frac{1}{3} + \frac{2}{3} \frac{J(J+1) - 3m^2}{(2J+3)(2J-1)}
\]  

(8)
In the quantum case, the continuous distribution of the angles $\gamma$ is replaced by a set of discrete lines, each of them weighted by the population of the state $|J, m\rangle$. Fig. 2 shows the distribution of $A_{J,m}$ in the thermal case for various values of the dimensionless parameter $J_T = \sqrt{k_B T/(\hbar B c)}$ that represents the typical "thermal" value of $J$ (for $J_T \geq 1$).

![Figure 2: Quantum distribution of $A_{J,m}$ in the thermal case. Panels (a) and (b) correspond to $J_T = 5$ and $J_T = 15$, respectively. Histogram in panel (c) presents a coarse-grained continuous normalized distribution of $A_{J,m}$ produced from (b) by averaging over a set of finite bins.]

The distribution of discrete values of $A_{J,m}$ demonstrates a non-trivial pattern, however it shows the expected unimodal rainbow feature (see Eq. (10)) for large enough $J_T$ after the coarse-grained averaging.

If the molecules are subject to a strong femtosecond pre-aligning pulse, the corresponding interaction potential is given by Eq. (11), in which $E(t)$ is replaced by the envelope $e(t)$ of the femtosecond pulse. If the pulse is short compared to the typical periods of molecular rotation, it may be considered as a delta-pulse. In the impulsive approximation, one obtains the following relation between the angular wavefunction before and after the pulse applied at $t = 0$:

$$\Psi(t = 0^+) = \exp(iP \cos^2 \theta) \Psi(t = 0^-), \quad (9)$$

where the kick strength, $P$ is given by $P = (1/4\hbar) \cdot (\alpha\| - \alpha\perp) \int_{-\infty}^\infty e^2(t) dt$. Here we assumed the vertical polarization (along $z$-axis) of the pulse. Physically, the dimensionless kick strength, $P$ equals to the typical amount of angular momentum (in the units of $\hbar$) supplied by the pulse to the molecule. For the vertical polarization of the laser field, $m$ is a conserved quantum number. This allows us to consider the excitation of the states with different initial $m$ values separately. In order to find $\Psi(t = 0^+)$ for any initial state, we introduce an artificial parameter $\xi$ that will be assigned the value $\xi = 1$ at the end of the calculations, and define

$$\Psi_\xi = \exp \left[ (iP \cos^2 \theta) \xi \right] \Psi(t = 0^-) = \sum_J c_J(\xi)|J, m\rangle, \quad (10)$$

By differentiating both sides of Eq. (10) with respect to $\xi$, we obtain the following set of differential equations for the coefficients $c_J$:

$$\dot{c}_J = iP \sum_J c_J(J', m) \cos^2 \theta|J, m\rangle, \quad (11)$$

where $\xi = dc/d\xi$. The diagonal matrix elements in Eq. (11) are given by Eq. (3), the off-diagonal ones can be found using recurrence relations for the spherical harmonics [13]. Since $\Psi_{\xi=0} = \Psi(t = 0^-)$ and $\Psi_{\xi=1} = \Psi(t = 0^+)$ (see Eq. (10)), we solve numerically this set of equations from $\xi = 0$ to $\xi = 1$, and find $\Psi(t = 0^+)$. In order to consider the effect of the field-free alignment at thermal conditions, we repeated this procedure for every initial $|J_0, m_0\rangle$ state. To find the modified population of the $|J, m\rangle$ states, the corresponding contributions from different initial states were summed together weighted with the Boltzmann’s statistical factors. For symmetric molecules, statistical spin factor should be taken into account. For example, for CS$_2$ molecules in the ground electronic and vibrational state, only even $J$ values are allowed due to the permutation symmetry for the exchange of two Bosonic Sulfur atoms (that have nuclear spin 0).

![Figure 3: Distribution of $A_{J,m}$ for molecules pre-aligned with the help of a short laser pulse polarized in the $x$ direction. The left column (a-b) presents directly the $A_{J,m}$ values, while the right column (c-d) shows the corresponding coarse-grained histograms (as in Fig. 2c). Panels (a) and (c) are calculated for $J_T = 5$ and $P = 5$; (b) and (d) are for $J_T = 5$ and $P = 25$. Using this technique, we considered deflection of initially thermal molecules that were pre-aligned with the help of short pulses polarized in $x$ and $z$ directions (Figs. 3a and 4 respectively). In the case of the alignment perpendicular to the deflecting field, the coarse-grained distribution...](image-url)
of $A_{J,m}$ (and that of the deflection angles) exhibits the *bimodal rainbow* shape, Eq. (7) for strong enough kicks ($P \gg 1$ and $P \gg J_T$). Finally, and most importantly, pre-alignment in the direction parallel to the deflecting field allows for almost complete removal of the rotational broadening. A considerable narrowing of the distribution can be seen when comparing Fig. 2b and Figs. 4b and 4c.

Our results indicate that pre-alignment provides an effective tool for controlling the deflection of rotating molecules, and it may be used for increasing the brightness of the scattered molecular beam. This might be important for nano-fabrication schemes based on the molecular optics approach [3]. Moreover, molecular deflection by non-resonant optical dipole force is considered as a promising route to separation of molecular mixtures (for a recent review, see [14]). Narrowing the distribution of the scattering angles may substantially increase the efficiency of separation of multi-component beams, especially when the pre-alignment is applied selectively to certain molecular species, such as isotopes [13], or nuclear spin isomers [15, 16]. More complicated techniques for pre-shaping the molecular angular distribution may be considered, such as confining molecular rotation to a certain plane by using the "optical molecular centrifuge" approach [18], double-pulse ignited "molecular propeller" [19], or two-direction alignment alternation excited by elliptic laser pulses [20]. In this case, a narrow angular peak is expected in molecular scattering, whose position is controllable by inclination of the plane of rotation with respect to the deflecting field. Laser pre-alignment may be used to manipulate molecular deflection by inhomogeneous static fields as well (for recent exciting experiments on post-alignment of molecules scattered by static electric fields see [21]). In particular, one may affect molecular motion in relatively weak fields that are insufficient to modify rotational states by themselves. Moreover, the same mechanisms may prove efficient for controlling inelastic molecular scattering off metallic/dielectric surfaces. These and other aspects of the present problem are subjects of an ongoing investigation.

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