Deflection of Field-Free Aligned Molecules

E. Gershnabel and I. Sh. Averbukh
Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

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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. We show that by preshaping 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 [1–3]. By controlling molecular translational degrees of freedom [4], novel elements of molecular optics can be realized, including molecular lens and molecular prism [1,2]. 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 [5,6]. This adds a new ingredient for controlling molecular trajectories [3,4], 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 preshaping 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 wave packets, 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., [7,8]). 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 [9–11]. We demonstrate that the average scattering angle of deflected molecules and its distribution may be dramatically modified by a proper field-free prealignment. 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 brings to mind the experiment by Stapelfeldt *et al.* [1] 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 the z direction) of a linear molecule moving in the 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 $E = E_0 \exp[-(x^2 + z^2)/\omega_0^2] \times \exp[-2\ln 2t^2/\tau^2]$. The interaction potential of a linear molecule in the laser field is given by

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

where E is defined above, and $\alpha_\parallel$ and $\alpha_\perp$ are the components of the molecular polarizability along the molecular axis, and perpendicular to it, respectively. Here θ 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 the 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

$$v_z = \frac{1}{M}\int_{-\infty}^{\infty} F_z(t)dt = -\frac{1}{M}\int_{-\infty}^{\infty} (\vec{\nabla} U(t))_z. \qquad (2)$$

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 θ 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 $T = 5$ K, which are subject to the deflecting field of 3×10^9 W/cm^2. The corresponding alignment potential $U \approx -\frac{1}{4}(\alpha_\parallel - \alpha_\perp)E_0^2 \approx 0.04$ 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, $\gamma = v_z/v_x$:

$$\gamma = \gamma_0[\alpha_\parallel \mathcal{A} + \alpha_\perp(1 - \mathcal{A})]/\bar{\alpha}. \tag{3}$$

Here $\bar{\alpha} = 1/3\alpha_\parallel + 2/3\alpha_\perp$ is the orientation-averaged molecular polarizability, and $\mathcal{A} = \overline{\cos^2\theta}$ 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 leads to the randomization of the deflection process. The constant γ_0 presents the average deflection angle for an isotropic molecular ensemble, and it is determined by the deflection scheme [1,12]. We provide below some heuristic classical arguments on the anticipated statistical properties of $\mathcal{A}$ and γ (both for thermal and prealigned 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).

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

$$\mathcal{A} = \overline{\cos^2\theta} = \tfrac{1}{2}\sin^2\theta_J. \tag{4}$$

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 $\langle\gamma\rangle = \gamma_0$. Equation (4) allows us to obtain the distribution function, $f(\mathcal{A})$ for $\mathcal{A}$ (and the related deflection angle) from the known isotropic distribution for θ_J. Since the inverse function $\theta_J(\mathcal{A})$ is multivalued, one obtains

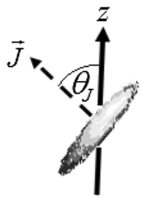

FIG. 1. A molecule rotates with the angular momentum $\vec{J}$ forming an angle θ_J with the laboratory z axis.

$$f(\mathcal{A}) = \sum_{i=1}^{2} \frac{1}{2}\sin\theta_J^{(i)} \left|\frac{d\mathcal{A}}{d\theta_J^{(i)}}\right|^{-1} = \frac{1}{\sqrt{1 - 2\mathcal{A}}}, \tag{5}$$

where we summed over the two branches of $\theta_J(\mathcal{A})$. This formula predicts a unimodal rainbow singularity in the distribution of the scattering angles at the maximal value $\gamma = \gamma_0(\alpha_\parallel + \alpha_\perp)/2\bar{\alpha}$ (for $\mathcal{A} = 1/2$), and a flat step near the minimal one $\gamma = \gamma_0\alpha_\perp/\bar{\alpha}$ (for $\mathcal{A} = 0$). Assume now that the molecules are prealigned 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 the x 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 θ_J becomes uniformly distributed in the interval $[0, \pi]$ with probability density $d\theta_J/\pi$. The corresponding probability distribution for $\mathcal{A}$ takes the form

$$f(\mathcal{A}) = \frac{\sqrt{2}}{\pi}\frac{1}{\sqrt{\mathcal{A}(1 - 2\mathcal{A})}}. \tag{6}$$

In contrast to Eq. (5), formula Eq. (6) 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 prealigned by a short strong laser pulse polarized parallel to the direction of the deflecting field (along the z axis). Such a pulse forces molecules to rotate in vertical planes, so that the vector of the angular momentum is preferentially confined to the horizontal xy plane [$\theta_J = \pi/2$, and $\mathcal{A} = 1/2$, see Eq. (4)]. In this way, the molecules experience the maximally possible time-averaged deflecting force which is the same for all the particles of the ensemble. This reduces dramatically the dispersion of the scattering angle γ defined by Eq. (3). The distribution of γ transforms to a narrow peak (asymptotically—a δ function) near the maximal value, $\gamma = \gamma_0(\alpha_\parallel + \alpha_\perp)/2\bar{\alpha}$.

For a more quantitative treatment, we consider quantum mechanically the deflection of a linear molecule described by the Hamiltonian $\mathcal{H} = \hat{J}^2/(2I)$. Here $\hat{J}$ is the operator of angular momentum, and I is the moment of inertia, which is related to the molecular rotational constant, $B = \hbar/(4\pi Ic)$ (c is the speed of light). For weak enough deflecting field, the scattering angle for a molecule in the $|J, m\rangle$ rotational state is given by Eq. (3), in which $\mathcal{A}$ is replaced by

$$\mathcal{A}_{J,m} = \langle J, m|\cos^2\theta|J, m\rangle = \frac{1}{3} + \frac{2}{3}\frac{J(J+1) - 3m^2}{(2J+3)(2J-1)}. \tag{7}$$

In the quantum case, the continuous distribution of the angles γ is replaced by a set of discrete lines, each of them weighted by the population of the state $|J, m\rangle$.

Figure 2 shows the distribution of $\mathcal{A}_{J,m}$ in the thermal case for various values of the dimensionless parameter $J_T = \sqrt{k_B T/(hBc)}$ that represents the typical "thermal" value of J (for $J_T \geq 1$). For CS_2 molecules, the values of $J_T = 5, 15$ correspond to $T = 3.9$ K and $T = 35$ K, respectively.

The distribution of discrete values of $\mathcal{A}_{J,m}$ demonstrates a nontrivial pattern. In particular, the values exceeding the classical limit 0.5 correspond to the states $|J, m = 0\rangle$ [see Eq. (7)], and they rapidly approach that limit as J grows. After the coarse-grained averaging, however, the distribution shows the expected unimodal rainbow feature [see Eq. (5)] for large enough J_T.

If the molecules are subject to a strong femtosecond prealigning pulse, the corresponding interaction potential is given by Eq. (1), in which $E(t)$ is replaced by the envelope $\epsilon(t)$ of the femtosecond pulse. In the impulsive approximation (''delta pulse''), one obtains the following relation between the angular wave function before and after the pulse applied at $t = 0$:

$$\Psi(t = 0^+) = \exp(iP\cos^2\theta)\Psi(t = 0^-), \tag{8}$$

where the kick strength P is given by $P = (1/4\hbar)(\alpha_\parallel - \alpha_\perp)\int_{-\infty}^{\infty}\epsilon^2(t)dt$. Here we assumed the vertical polarization (along the z axis) of the pulse. Physically, the dimensionless kick strength P is equal to the typical amount of angular momentum (in the units of $\hbar$) supplied by the pulse to the molecule. For example, in the case of CS_2 molecules, the values of $P = 5$, 25 correspond to the excitation by 0.5 ps (FWHM) laser pulses with the maximal intensity of 4.6×10^{11} W/cm^2 and 2.3×10^{12} W/cm^2, respectively. For the vertical polarization of the laser field, m is a conserved quantum number. In order to find $\Psi(t = 0^+)$ for any initial state, we introduce an artificial parameter ξ that will be assigned the value $\xi = 1$ at the end of the calculations, and define

$$\Psi_\xi = \exp[(iP\cos^2\theta)\xi]\Psi(t = 0^-) = \sum_J c_J(\xi)|J, m\rangle. \tag{9}$$

By differentiating both sides of Eq. (9) with respect to ξ, we obtain the following set of differential equations for the coefficients c_J:

$$\dot{c}_{J'} = iP\sum_J c_J\langle J', m|\cos^2\theta|J, m\rangle, \tag{10}$$

where $\dot{c} = dc/d\xi$. The diagonal matrix elements in Eq. (10) are given by Eq. (7), the off-diagonal ones can be found using recurrence relations for the spherical harmonics. To find $\Psi(t = 0^+)$, we solve numerically this set of equations from $\xi = 0$ to $\xi = 1$. 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 have to be summed together weighted with the Boltzmann's statistical factor, and taking into account the spin-statistical factor in the case of symmetric molecules. Using this technique, we considered deflection of initially thermal molecules that were prealigned with the help of short pulses polarized in x and z directions (Figs. 3 and 4, respectively). In the case of the alignment perpendicular to the deflecting field, the coarse-grained distribution of $\mathcal{A}_{J,m}$ (and that of the deflection angles) exhibits the bimodal rainbow shape, Eq. (6) for strong enough kicks ($P \gg 1$ and $P \gg J_T$). Most importantly, prealignment 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. 2(a) and Figs. 4(b) and 4(d). The conditions required for the considerable narrowing shown at Fig. 4(d) correspond to the maximal degree of field-free

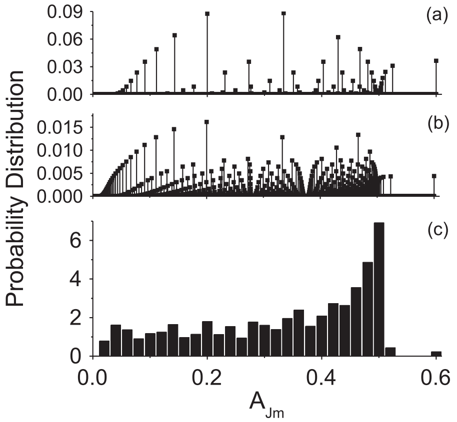

FIG. 2. Quantum distribution of $\mathcal{A}_{J,m}$ in the thermal case. Panels (a) and (b) correspond to $J_T = 5$ and $J_T = 15$, respectively. The histogram in panel (c) shows a coarse-grained version of the distribution in panel (b)

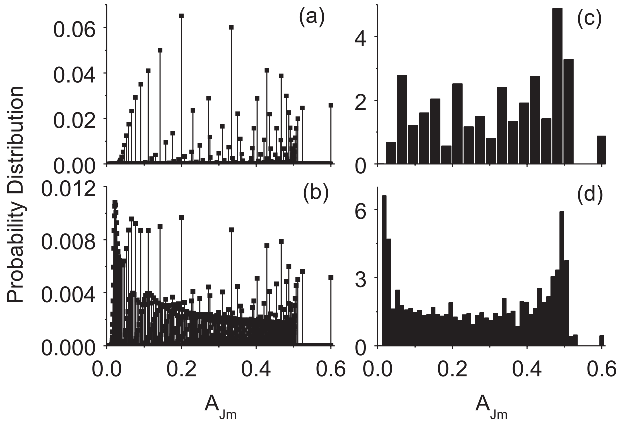

FIG. 3. Distribution of $\mathcal{A}_{J,m}$ for molecules prealigned with the help of a short laser pulse polarized in the x direction. The left column (a),(b) presents directly the $\mathcal{A}_{J,m}$ values, while the right column (c),(d) shows the corresponding coarse-grained histograms [as in Fig. 2(c)]. Panels (a) and (c) are calculated for $J_T = 5$ and $P = 5$; (b) and (d) are for $J_T = 5$ and $P = 25$.

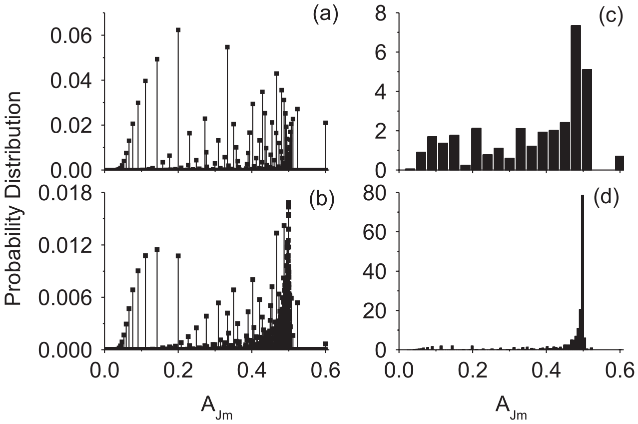

FIG. 4. Distribution of $\mathcal{A}_{J,m}$ for molecules prealigned in the z direction. The left column (a),(b) presents directly the $\mathcal{A}_{J,m}$ values, while the right column (c),(d) shows the corresponding coarse-grained histograms. Panels (a) and (c) are calculated for $J_T = 5$ and $P = 5$; (b) and (d) are for $J_T = 5$ and $P = 25$.

prealignment $\langle\cos^2\theta\rangle_{\max} = 0.7$. This can be readily achieved with the current experimental technology, even at room temperature [13]. We analyzed in detail the above narrowing phenomenon [12], and derived an asymptotic expression $(\Delta\mathcal{A})^2 = (\sqrt{\pi}/32)(J_T/P)$ for the variance of the distribution. This estimate for the width $\Delta\mathcal{A}$ is formally valid for $J_T \geq 1$ and $P \gg J_T$, and it coincides within the 10% accuracy with the exact quantum results for $P = 25$ and $J_T = 5$ presented above.

Our results indicate that prealignment 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 nanofabrication schemes based on the molecular optics approach [4]. Moreover, molecular deflection by nonresonant optical dipole force is considered as a promising route to the 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 multicomponent beams, especially when the prealignment is applied selectively to certain molecular species, such as isotopes [15], or nuclear spin isomers [16,17]. More complicated techniques for preshaping 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 planar alignment by perpendicularly polarized 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 prealignment may be used to manipulate molecular deflection by inhomogeneous static fields as well (for recent exciting experiments on postalignment of molecules scattered by static electric fields, see [21]). Moreover, the same mechanisms may prove efficient for controlling inelastic molecular scattering off metallic or dielectric surfaces. These and other aspects of the present problem are subjects of an ongoing investigation.

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