Electric deflection of rotating molecules

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We provide a theory of the deflection of polar and nonpolar rotating molecules by inhomogeneous static electric field. Rainbowlike features in the angular distribution of the scattered molecules are analyzed in detail. Furthermore, we demonstrate that one may efficiently control the deflection process with the help of short and strong femtosecond laser pulses. In particular, the deflection process may be turned off by a proper excitation, and the angular dispersion of the deflected molecules can be substantially reduced. We study the problem both classically and quantum mechanically, taking into account the effects of strong deflecting field on the molecular rotations. In both treatments we arrive at the same conclusions. The suggested control scheme paves the way for many applications involving molecular focusing, guiding, and trapping by inhomogeneous fields.

I. INTRODUCTION

Deflection of molecules by inhomogeneous external fields is an important subject of molecular physics, which continues to attract a lot of attention in recent years.1–7 The external fields can be magnetic or electric,1–4 or even optical fields of strong lasers.5–12 By controlling molecular translational motion with external fields, novel elements of molecular optics can be realized, including molecular lens5, 6 and molecular prism.7 Deflection by external fields is also used as a tool to measure molecular polarizability4 and molecular dipole moment. The mechanism of molecular deflection by a nonuniform static electric field is rather clear. For a nonpolar molecule, the field induces molecular polarization, interacts with it, and deflects the molecules along the interaction energy gradient. For a polar molecule, the field interacts with the molecular permanent dipole moment as well. As most molecules have anisotropic polarizability or and a permanent dipole moment, the deflecting field depends on the molecular orientation with respect to the deflecting field. Previous studies on 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 (or dipole moment). This dispersion was observed via broadening of the scattered molecular beam, and was reported in the “two-wire” electric field experiments4, 13, 14 and also in the multipole electric field experiments.15–17 More recently, this kind of rotation-induced dispersion in molecular scattering by static electric fields was used as a selection tool in experiments on laser-induced molecular alignment.18 The field-molecule interactions become intensity-dependent for strong enough fields due to the field-induced modification of the molecular angular motion.19, 20 This adds a new ingredient for controlling molecular trajectories.8, 9, 12, 20, 21

Recently, we showed that molecular deflection by strong fields of focused laser beams can be significantly affected and controlled by preshaping molecular angular distribution before the molecules enter the interaction zone.22 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 reviews on field-free alignment, see, e.g., Refs. 23 and 24). 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.25–27

In the present paper we extend this approach to molecular deflection in static electric fields, and demonstrate that the average scattering angle of deflected molecules and its distribution may be dramatically modified by a proper field-free prealignment with ultra-fast lasers. An important difference between the scattering in a static field and an optical field22 is due to the role of the molecular permanent dipole moment. Dipole interaction with the laser beams averages to zero because of the fast oscillations of the optical fields, however this kind of interaction becomes dominant for polar molecules placed in the static electric fields. In the present paper, we analyze in detail interaction of rotating molecules with the static electric fields (taking into account both the dipole-type and polarization-type interactions), and demonstrate that laser-induced prealignment provides a flexible tool for controlling molecular motion in these fields.

In Sec. II we present the deflection scheme, and provide heuristic arguments on the anticipated role of molecular rotation on the scattering process (both for thermal molecules and molecules prealigned by additional laser pulses). In Sec. III we provide a full classical treatment of the problem, which supports the heuristic predictions of Sec. II. An alternative classical analysis based on the formalism of adiabatic invariants is given in the Appendix, and it leads to the same results. In Sec. IV we support our control approach by means of a
full-scale quantum mechanical analysis. Finally, we summarize our results in Sec. V.

II. MOLECULAR DEFLECTION

We consider a deflection scheme that is based on the interaction between a linear molecule and an inhomogeneous static electric field. In particular, we follow the lines of experiments, in which a collimated particle beam goes through a long deflector made of two cylindrical electrodes’ faces. Electrical field $E$ between the two poles is equivalent to an “electrical two-wire field.” This geometry allows to obtain an electric field $E$ and a field gradient $dE/dz$ which are nearly constant over the width of the collimated molecular beam (see Fig. 1).

The interaction potential of a linear molecule in the static field is given by

$$U = -\frac{1}{2}E^2 (\Delta \alpha \cos^2 \theta + \alpha_\perp) - \mu E \cos \theta,$$

where $E$ is the electric field; $\alpha_\parallel$ and $\alpha_\perp$ are the components of the molecular polarizability along the molecular axis, and perpendicular to it, respectively; and $\mu$ is the permanent dipole moment. Here $\theta$ is the angle between the electric field direction (along the laboratory $z$ axis) and the molecular axis. A molecule initially moving along the $x$ direction acquires a velocity component $v_x$ along $z$ direction. We consider the perturbation regime corresponding to a small deflection angle, $\gamma \approx v_z/v_x$ and, therefore, assume the molecules are subject to the fixed values of the field and field gradient ($E$ and $\nabla E$, respectively) inside the deflector.

The deflection velocity is given by

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

(2)

where $M$ is the mass of the molecules. The time-dependence of the force (and of the potential $U$) in Eq. (2) comes from two sources: projectile motion of the molecule through the deflector, and time variation of the angle $\theta$ due to molecular rotation. For simplicity, we neglect the edge effects at the entrance and exit of the deflector.

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,

$$\gamma = \frac{v_z/v_x}{\gamma_0},$$

$$\gamma = \left\{ E \left[ \alpha_\parallel A_2 + \alpha_\perp (1 - A_2) \right] + \mu A_1 \right\} \frac{t_d \nabla E}{Mv_x}.$$  

(3)

Here $A_{1,2} \equiv \cos^{1,2} \theta$ denotes the time-averaged value of $\cos^{1,2} \theta$, and $t_d$ is the passage time through the deflector. The quantities $A_{1,2}$ depend on the relative orientation of the vector of angular momentum and the direction of the deflecting field. It is different for different molecules of the incident ensemble, which leads to the randomization of the deflection process.

We provide below some heuristic classical arguments on the anticipated statistical properties of $A_{1,2}$. We start with the simplest case of a linear molecule, which is polarizable, but has no permanent dipole moment, i.e., $\Delta \alpha \neq 0$, $\mu = 0$ (for some relevant experiments on deflecting such molecules, see, for instance, Refs. 4 and 5). For illustrative purposes, we consider here only the deflection of such a molecule by a weak field that does not disturb significantly the molecular rotation (a complete study including the thorough analysis of the effects of strong deflecting field was done in our recent paper). This molecule rotates freely in a plane perpendicular to the vector $\vec{J}$ of the angular momentum (see Fig. 2).

The projection of the molecular axis on the vertical $z$ direction is given by

$$\cos \theta(t) = \cos(\omega t) \sin \theta_f,$$

where $\theta_f$ is the angle between $\vec{J}$ and $z$ axis, and $\omega$ is the angular frequency of molecular rotation.

By averaging Eq. (4) over time, we obtain

$$A_1 = \overline{\cos \theta} = 0,$$

$$A_2 = \overline{\cos^2 \theta} = \frac{1}{2} \sin^2 \theta_f.$$  

(5)

For random and isotropic orientation of vector $\vec{J}$ in space, the probability density for $\theta_f$ distribution is $1/2 \sin(\theta_f)$. The mean value of the deflection angle is then $\langle \gamma \rangle = \gamma_0$, where the constant $\gamma_0$ presents the average deflection angle for an isotropic molecular ensemble:

$$\gamma_0 = \left[ \frac{1}{3} \alpha_\parallel + \frac{2}{3} \alpha_\perp \right] \frac{E \nabla E t_d}{Mv_x}.$$  

(6)

FIG. 1. The deflection scheme. Linear molecules, initially moving in the $x$ direction (with velocity $v_x$), enter a static electric field (directed along the $z$ axis). They are deflected by the field gradient, and get the deflection velocity $v_z$.

FIG. 2. A molecule rotates with a given angular momentum $\vec{J}$ that is randomly oriented in space. $\theta_f$ is the angle between the angular momentum and the laboratory $z$ axis.
where we summed over the two branches of \( \theta f(A_2) \). This formula predicts a unimodal rainbow singularity in the distribution of the scattering angles at the maximal value \( \gamma = \gamma_0(\alpha_{||} + \alpha_\perp)/2\pi \) (for \( A_2 = 1/2 \)), and a flat step near the minimal one \( \gamma = \gamma_0\alpha_\perp/\alpha \) (for \( A_2 = 0 \)). Here \( \alpha \equiv 1/3\alpha_{||} + 2/3\alpha_\perp \) is the orientation-averaged molecular polarizability. These results are similar to the ones derived by us previously for molecular scattering by oscillating optical fields.\(^{22}\)

As the next example, we consider the opposite case of polar molecules with \( \mu \neq 0 \) and negligible polarization-type interaction. We will consider both low and high deflecting fields, and for the sake of simplicity, we start with a 2D model, i.e., for a molecule that rotates with no azimuthal momentum. The full 3D consideration at thermal conditions will be provided after that. The 2D model allows for a complete analytical treatment, and it demonstrates many of the features present in the 3D case. Moreover, it adequately describes behavior of the molecules prealigned by a short laser pulse before entering the deflection field (the problem we consider later in this paper). In the limit of \( \mathcal{H}/\mu \mathcal{E} \ll 1 \) (\( \mathcal{H} \) is the molecular energy), the molecular axis is trapped by the electric field, and \( A_1 \approx 1 \). As \( \mathcal{H} \) is increased, the molecules may still be trapped, but with \( A_1 < 1 \). For angularly trapped molecules with high enough \( \mathcal{H} \), the quantity \( A \) becomes negative, i.e., \( A_1 < 0 \). The latter happens because such molecules spend most of the time being against the electric field when performing nonlinear angular oscillations. As the energy is increased even more, the molecules become untrapped, and start performing full rotations. In this case, we expect that \( A_1 < 0 \) due to the same reason: the molecules accelerate their rotation when the dipole moment tends to be parallel to the electric field, and they decelerate it when the dipole moment looks against the field. As a result, the time-averaged value of \( \cos \theta \) is negative. Considering 2D molecular rotation in the presence of the electric field, we can write:

\[
dt = \sqrt{\frac{I}{2}} \frac{d\theta}{\sqrt{\mathcal{H} + \mu \mathcal{E} \cos \theta}},
\]

where \( I \) is the moment of inertia. Assuming the untrapped regime (\( \mu \mathcal{E}/\mathcal{H} < 1 \)), the rotation period is given by\(^{30}\)

\[
T_{\text{period}} = \sqrt{\frac{I}{2}} \int_{0}^{\pi} \frac{d\theta}{\sqrt{\mathcal{H} + \mu \mathcal{E} \cos \theta}} = \sqrt{\frac{I}{2}} \frac{2}{\sqrt{\mathcal{H} + \mu \mathcal{E}}} F\left(\frac{\pi}{2}, r\right).
\]

The time-averaged value of \( \cos \theta \) is

\[
A_1 = \frac{4}{T_{\text{period}}} \int_{0}^{\pi} \frac{d\theta}{\sqrt{\mathcal{H} + \mu \mathcal{E} \cos \theta}} \cos \theta,
\]

\[
= \left( \frac{\mathcal{H}}{\mu \mathcal{E}} + 1 \right) \frac{E\left(\frac{\pi}{2}, r\right)}{F\left(\frac{\pi}{2}, r\right)} - \frac{a}{b}.
\]

Here \( r \equiv \sqrt{2\mu \mathcal{E}/(\mathcal{H} + \mu \mathcal{E})} \). The functions \( E(\pi/2, r) \) and \( F(\pi/2, r) \) are the first and second order elliptic integral, respectively. From Eq. (10) we learn that \( A_1 \approx -\mu \mathcal{E}/4 \mathcal{H} \) in the limit of weak fields, \( \mu \mathcal{E}/\mathcal{H} \ll 1 \). This value is negative, as discussed above.

Summarizing, in the 2D approximation, \( A_1 = 1 \) when \( \mathcal{H}/\mu \mathcal{E} \ll 1 \), it is close to 0 when \( \mu \mathcal{E}/\mathcal{H} \ll 1 \), and it takes negative values in-between. This assumes the existence of a negative minimum of \( A_1 \) as a function of \( \mathcal{H}/\mu \mathcal{E} \).

The properties of the \( A_2 \) quantity are somehow different in the considered 2D model. For low \( \mathcal{H} \), the molecular rotation is suppressed, and \( A_2 = 1 \). The period of angular oscillations of the trapped molecules (\( \mu \mathcal{E}/H > 1 \)) is given by

\[
T_{\text{period}} = \frac{4}{I} \int_{0}^{\pi} \cos^{-1}(-H/\mu \mathcal{E}) \frac{d\theta}{\sqrt{\mathcal{H} + \mu \mathcal{E} \cos \theta}}.
\]

The time-averaged value of \( \cos^2 \theta \) is

\[
A_2 = \frac{4}{T_{\text{period}}} \int_{0}^{\pi} \cos^{-1}(-H/\mu \mathcal{E}) \frac{d\theta \cos^2 \theta}{\sqrt{\mathcal{H} + \mu \mathcal{E} \cos \theta}} = \frac{2}{3} \frac{\mathcal{H}}{\mu \mathcal{E}} + \frac{1}{3} - \frac{4}{3} \frac{\mathcal{H}}{\mu \mathcal{E}} \frac{E\left(\frac{\pi}{2}, r\right)}{F\left(\frac{\pi}{2}, r\right)},
\]

where \( r, E(\pi/2, 1/r) \), and \( F(\pi/2, 1/r) \) were defined above.

The function in Eq. (12) has a local minimum at \( A_2 = 0.279 \), which suggests a rainbow peak in the distribution of \( A_2 \) in the case of a smooth distribution of the parameter \( \mathcal{H}/\mu \mathcal{E} \). For high enough energy, the molecules rotate almost as free rotors, and we expect a rainbow peak in the \( A_2 \) distribution at \( A_2 = 0.5 \), as was suggested by Eq. (7).

Finally, in order to complete our analysis, we consider the field-affected molecular rotation in 3D case, find numerically and plot the quantities of \( A_{1,2} \) (Figs. 3 and 4, respectively) for different values of dimensionless rotational energy and azimuthal canonical momentum (the details of the calculations can be found in Sec. III). For the lowest possible negative values of the total energy, \( \mathcal{H} \) both plots demonstrate angular trapping (\( A_1 = 1, A_2 = 1 \)). For small values of the azimuthal momentum we observe a negative minimum (around \( \mathcal{H} \approx \mu \mathcal{E} \)) of \( A_1 \), the nature of which has been already discussed. In this limit, we also observe a minimum at \( A_2 = 0.274 \) and a peak at \( A_2 = 0.5 \), which is in agreement with the previous 2D model. For high rotational energies (and high azimuthal momentum), \( A_1 \approx 0 \). Finally, for high azimuthal momentum we also
observe a strong decrease in the $A_2$ values, since the molecules mainly rotate in the $xy$ plane in this limit.

III. CLASSICAL TREATMENT

Consider a classical rigid rotor (linear molecule) described by the Lagrangian:

$$ L = \frac{I}{2} (\dot{\phi}^2 \sin^2 \theta + \dot{\theta}^2) + \frac{1}{2} \mathcal{E}^2 \left( \Delta \alpha \cos^2 \theta + \alpha_\perp \right) + \mu \mathcal{E} \cos \theta, \quad (13) $$

where $\theta$ and $\phi$ are Euler angles, and $I$ is the moment of inertia. The canonical momentum for the $\phi$ angle

$$ P_\phi = I \dot{\phi} \sin^2 \theta \quad (14) $$

is a constant of motion as $\phi$ is a cyclic coordinate. The canonical momentum $P_\theta$ is given by

$$ P_\theta = I \dot{\theta}. \quad (15) $$

The Euler–Lagrange equation for the $\theta$ variable is

$$ \frac{d}{dt} \frac{\partial L}{\partial \dot{\theta}} - \frac{\partial L}{\partial \theta} = 0, \quad (16) $$

which leads to

$$ \frac{d^2 \theta}{dt^2} = \frac{P_\theta}{I} \cos \theta \sin^2 \theta - \frac{\mathcal{E}^2 \Delta \alpha}{I} \sin \theta \cos \theta - \frac{\mu \mathcal{E}}{I} \sin \theta. \quad (17) $$

When considering a thermal ensemble of molecules, it is convenient to switch to dimensionless variables, in which the canonical momenta are measured in the units of $P_{th} = I \omega_{th}$, with $\omega_{th} = \sqrt{k_B T}$, where $T$ is the temperature and $k_B$ is the Boltzmann’s constant. By setting $P_\phi^\prime = P_\phi / P_{th}$, $P_\theta^\prime = P_\theta / P_{th}$, and $t^\prime = \omega_{th} t$, Eq. (17) becomes

$$ \frac{d^2 \theta}{dt^2} = P_\theta^\prime \cos \theta \sin^2 \theta - C \sin \theta \cos \theta - D \sin \theta, \quad (18) $$

where $C \equiv \mathcal{E}^2 \Delta \alpha / (k_B T)$ and $D \equiv \mu \mathcal{E} / (k_B T)$.

Considering a deflecting field that is adiabatically increasing to its final value $\mathcal{E}$ (adiabatic with respect to the molecular rotational dynamics), we numerically solve Eq. (18) and find the time-dependent values of $\cos \theta(t)$ and $\cos^2 \theta(t)$.

In order to find the $A_{1,2}$, we calculate

$$ A_{1,2}(t) = \frac{1}{t - t_\varepsilon} \int_{t_\varepsilon}^{t} \cos^{1/2} \theta dt \quad (19) $$

and consider $A_{1,2} = \cos^{1/2} \theta$ as the limit value to which $A_{1,2}(t)$ converges as $t - t_\varepsilon \to \infty$. Here $t_\varepsilon$ is the rising time in which the deflecting field reaches its maximal value $\mathcal{E}$.

The probability distribution of $A_{1,2}$ is given by

$$ f(A_{1,2}) = \int \int \int d\theta d\phi dP_\theta \rho(\theta) \rho(\phi) dP_\phi dP_\phi^\prime \rho(0) \times \delta(A_{1,2} - \cos^{1/2} \theta) \times f(\theta(0), \phi(0), P_\theta(0), P_\phi(0), P_\phi^\prime(0)), \quad (20) $$

where

$$ f = \frac{1}{8 \pi^2} \exp \left[ -\frac{1}{2} \left( P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta} \right) \right] \quad (21) $$

is the thermal distribution function.

A. Deflection of thermal molecules

Using this approach, we considered distribution functions for $A_{1,2}$ (and corresponding distributions of the deflection angle $\gamma$) for a thermal beam of $KCl$ molecules [\( \mu = 10.24 \, D, \, \alpha_\parallel = 5.95 \, \text{Å}^3, \, \alpha_\perp = 4.92 \, \text{Å}^3 \) (Ref. 32)]. For
the chosen rotational temperature \( T = 4.63 \, K \), the typical “thermal” value of the angular momentum is \( J_{T} = 5 \), where \( J_{T} = \sqrt{\frac{k_{B} T}{\hbar B r c}} \), \( B_{r} \) is the rotational constant, and \( c \) is the speed of light. We plot the distribution functions for moderate \((1.8 \times 10^{6} \, \text{V/m})\) and strong \((1.8 \times 10^{7} \, \text{V/m})\) values of the deflecting field at Figs. 5 and 6, respectively. For the moderate field, \( C = 5.81 \times 10^{-6} \) and \( D = 0.96 \), so that the dipole-field interaction is comparable with the typical thermal rotational energy, while the polarization-type interaction is negligible. In this case, a sizable portion of molecules are trapped by the field, which is reflected in the high positive values of \( A_{1} \) [Fig. 5(a)]. The untrapped molecules are performing full rotations, and they contribute to the negative values of \( A_{1} \). Figure 5(b) presents the distribution of \( A_{2} \), and it shows two rainbows (the first one at approximately 0.28, and the second one at 0.5), as is expected from the discussion in Sec. II. The distribution of the deflection angles (not shown here) is similar to the distribution of \( A_{1} \), as the contribution from the polarization-type interaction (proportional to \( A_{2} \)) is negligible in the considered numerical example. The \( A_{2} \) distribution for the \( KCl \) molecule may be directly measured in a deflection experiment that combines a homogeneous static field and an inhomogeneous laser field. The static field will define the distributions of \( A_{1} \) and \( A_{2} \), and the laser field will deflect the molecules according to the \( A_{1} \) values.\(^{22}\)

In the case of a strong field \((1.8 \times 10^{7} \, \text{V/m})\) shown at Fig. 6, \( D = 9.62 \), and \( C \) is still negligible. Now the dominant portion of molecules is highly trapped by the electric field, and the distribution of \( A_{1} \) is shifted accordingly to the higher positive values [Fig. 6(a)]. The rainbow at 0.5 in the \( A_{2} \) distribution [Fig. 6(b)] practically disappears due to the increased amount of molecules with the suppressed rotation.

Finally, in Fig. 7 we present the case of a strong deflecting field, but at higher temperature. Though the field is as strong as in Fig. 6, \( D \) value is similar to the one of Fig. 5, and the curves are correspondingly similar.

### B. Deflection of prealigned molecules

Now assume that the molecules are subject to a femtosecond prealigning pulse polarized in \( z \) direction at \( t = 0 \), before they enter the deflecting field. The interaction of molecular permanent dipole moment with the laser pulse averages to zero because of the fast optical oscillations. The polarization-type interaction is given by the first term in Eq. (1), in which \( \mathcal{E} \) is replaced by the envelope \( \epsilon \) of the femtosecond pulse, and an additional factor of 0.5 is added due to the oscillatory nature of the optical field. We assume that the pulse is short compared to the rotational period of the molecules, and consider it as a delta-pulse. The rotational dynamics of the laser-kicked molecules is then described by the same formalism as above, but with \( P_{\phi}(0) \) replaced by

\[
P_{\phi}^{' \prime}(0) \rightarrow P_{\phi}^{' \prime}(0) - P_{z}^{' \prime} \sin(2\theta(0)).
\]

Here \( P_{x}^{' \prime} = \frac{2\mathcal{E}}{\hbar k_{B} T T} \) is a properly normalized kick strength of the laser pulse, with \( \mathcal{P} \) given by

\[
P = (1/4\mathcal{E}) (\alpha_{||} - \alpha_{\perp}) \int_{-\infty}^{\infty} e^{2}(t) dt.
\]
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 example, in the case of $KCl$ molecules, $P = 25$ corresponds to the excitation by $2\,ps$ (FWHM) laser pulses with the maximal intensity of $5.8 \times 10^{12}$ W/cm$^2$. The distribution functions for kicked molecules are shown in Fig. 8. The kick parallel to the deflecting field increases the rotational energy of the molecules (i.e., makes them untrapped), while keeping unchanged the value of the azimuthal momentum. As was explained in Sec. II, untrapped molecules with relatively low azimuthal momentum contribute to the negative shift of the peak in the $A_1$ distribution function [Fig. 8(a)]. Since most of the molecules became untrapped, the rainbow around 0.5 in the distribution of $A_2$ becomes the dominant rainbow. For the numerical example under consideration, the distribution of the deflection angles has the same shape as the distribution for $A_1$ (with a proper scaling). As follows from Fig. 8(a), a prealigning laser pulse applied parallel to the direction of the deflecting field leads to a dramatic narrowing in the distribution of the scattering angles, and increases the brightness of the molecular beam deflected by a static electric field. Furthermore, strong enough pre-alignment may substantially reduce the scattering angles, which may turn off the deflection process.

In the case of an aligning pulse in the $x$ direction (perpendicular to the deflecting field), both $P_{\phi}'(0)$ and $P_\phi'(0)$ are replaced by

$$P_{\phi}'(0) \rightarrow P_{\phi}'(0) + P_\phi' \cos^2 \phi(0) \sin(2\theta(0)),$$

$$P_\phi'(0) \rightarrow P_\phi'(0) - P_\phi' \sin^2(\theta(0)) \sin(2\phi(0)).$$

The distribution functions for $A_{1,2}$ in this case are shown in Fig. 9. Such a pulse forces the molecules to rotate preferentially in the planes containing the $x$ axis. In a previous work, we showed that the distribution of $A_2$ has two rainbows at 0 and 0.5 in the absence of the static field. In the present case, as can be seen from Fig. 9(b), the distribution of $A_2$ still preserves the rainbow at 0.5, but the rainbow at 0 is smeared due to the effect of the strong deflecting field ($D = 9.62$). Nevertheless, we still may observe a considerable concentration of molecules at low $A_2$ values. The peak at $A_2 \approx 0.28$ is still present due to the reasons explained in Sec. II. The two rainbows are due to molecules that rotate with small azimuthal momentum. The distribution of $A_1$ [Fig. 9(a)] has now a strong peak at low positive $A_1$ values, since a great portion of the molecules is freely rotating with large azimuthal momentum provided by the laser kick.

Finally, before proceeding to the quantum treatment of the same problem, we refer the reader to the Appendix, in which an alternative approach to the classical calculation of $A_{1,2}$ is given by means of the formalism of adiabatic invariants.

**IV. QUANTUM TREATMENT**

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 prealigning pulses on the other hand, we consider quantum mechanically the deflection of a linear molecule described by the Hamiltonian:

$$\hat{H} = \frac{\vec{j}^2}{2I} - \mu E \cos \theta - \frac{1}{2} \vec{E}^2 \left[ (\alpha_\parallel - \alpha_\perp) \cos^2 \theta + \alpha_\perp \right],$$

where $J$ is the angular momentum operator.

Without the electric field $E$, the eigenfunctions of the free-space molecule are given by the free-rotor eigenfunctions $|J, m\rangle$. Before the molecules enter the deflecting field, we prealign them by a short femtosecond laser pulse. Such a pulse creates a rotational wave packet of the $|J, m\rangle$ states. After the prealigning laser pulse is over, the molecules enter adiabatically the region of the static field. Then, each $|J, m\rangle$ state (within the wave packet) transforms into the corresponding eigenstate $|J, m\rangle$, where $J$ is the quantum number associated adiabatically with the quantum number $J$. The relation between $|J, m\rangle$ and the free-rotor eigenfunctions may be described by

$$|J, m\rangle = \sum_{J=|m|}^{\infty} \beta_{J,m} |J, m\rangle.$$
The force, $\mathcal{F}$ acting on the molecule is given by

$$\mathcal{F} = -\nabla \mathcal{H} = -\frac{\partial \mathcal{H}}{\partial \mathcal{E}} \frac{d\mathcal{E}}{d\varepsilon}.$$  \hfill (27)

The first derivative is obtained by the means of the Hellman–Feynman theorem, that is being in an eigenstate $|J, m\rangle$,

$$\left. \frac{\partial \mathcal{H}_m(E)}{\partial \mathcal{E}} \right|_{E=\mathcal{E}} = \left( J, m \right| \hat{\partial} \mathcal{E} \left| J, m \right).$$  \hfill (28)

From Eqs. (25), (27), and (28) it is clear that the deflection angle of a molecule in a $|J, m\rangle$ state is given by Eq. (3), in which $A_{1,2}$ are replaced by

$$A_1^Jm = \left( J, m \right| \cos \theta |J, m\rangle,$$

$$A_2^Jm = \left( J, m \right| \cos^2 \theta |J, m\rangle.$$  \hfill (29)

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 thermal population of the state $|J, m\rangle$. Figure 10 shows the distributions of $A_{1,2}^Jm$ in the thermal case (i.e., without prealignment). These results can be compared to their classical analogs in Fig. 7, where the same structure is seen.

If the molecules are subject to a strong femtosecond prealigning pulse parallel to the deflecting field, the corresponding interaction potential is given, as in Sec. III, by Eq. (1), in which $\mathcal{E}$ is replaced by the envelope $\epsilon$ of the femtosecond pulse (including the 1/2 factor, as was explained in Sec. III). If the pulse is short compared to the typical periods of molecular rotation, it may be again considered as a delta-pulse. The validity of this approximation was studied in Ref. 33, in which the effect of the finite width of the pulses on the process of molecular alignment was examined in detail. In the impulsive approximation, one obtains the following relation between the angular wavefunction before and after the pulse applied at $t = 0$:

$$\Psi(t = 0^+) = \exp(iP \cos^2 \theta)\Psi(t = 0^-).$$  \hfill (30)

where the kick strength, $P$ is given by Eq. (23). For the polarization of the laser field along $z$ axis, $m$ 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

$$\Psi_{\xi} = \exp \left[ (iP \cos^2 \theta)\xi \right] \Psi(t = 0^-) = \sum_j c_j(\xi)|J, m\rangle.$$  \hfill (31)

By differentiating both sides of Eq. (31) with respect to $\xi$, we obtain the following set of differential equations for the coefficients $c_j$:

$$\dot{c}_J = iP \sum_j c_j(J', m| \cos^2 \theta |J, m\rangle,$$  \hfill (32)

where $\dot{c} = dc/d\xi$. The matrix elements in Eq. (32) can be found using recurrence relations for the spherical harmonics. Since $\Psi_{\xi=0} = \Psi(t = 0^-)$ and $\Psi_{\xi=1} = \Psi(t = 0^+)$ (see Eq. (31)), 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:

$$f(A_{J,m_0}) = \sum_{J, m} \frac{\exp(-\mathcal{H}_m/k_B T) Q_{rot}}{|c_j|^2 \delta_{A_{J,m_0} A_{J,m}}},$$  \hfill (33)

where $c_j$ are the coefficients [from Eq. (32)] of the wave packet that was excited from the initial state $|J_0, m_0\rangle$; $\delta$ is the Kronecker delta symbol, and $Q_{rot}$ is the rotational partition function. The distribution in the case of parallel prealignment is given in Fig. 11. The results are quite similar to the classical results from Fig. 8.

In the case of an aligning pulse in the $x$ direction, the operator in Eq. (30) becomes

$$\Psi(t = 0^+) = \exp(iP \cos^2 \phi \sin^2 \theta)\Psi(t = 0^-)$$  \hfill (34)

FIG. 10. Quantum distributions of (a) $A_1$ and (b) $A_2$ for a thermal beam of $KCl$ molecules in a strong field ($1.8 \times 10^7$ V/m) and $J_F = 15$ ($C = 6.46 \times 10^{-5}$; $D = 1.07$). These graphs are similar to the classical graphs of Fig. 7.

FIG. 11. Quantum distributions for prealigned $KCl$ molecules. Here the prealignment pulse ($P = 25$) was parallel to the deflecting field (strong field, $1.8 \times 10^7$ V/m; $C = 5.81 \times 10^{-5}$; $D = 9.62$). Temperature corresponds to $J_F = 5$. These graphs are similar to the classical graphs of Fig. 8.
and a procedure similar to the described above is used to find the deflection distribution (one should pay attention that \( m \) is no longer a conserved number during the operation of the pulse in the \( x \) direction). The distribution for the case of perpendicular prealignment is given in Fig. 12. These results are similar to the classical predictions from Fig. 9.

V. DISCUSSION AND CONCLUSIONS

In this work we considered molecular deflection by weak and strong inhomogeneous static electric fields. As the deflecting field is increased, it modifies the time-averaged alignment/orientation of the molecules. This affects the dipole force, and we have studied both classically and quantum mechanically the resulting deflection process. We found that laser-induced field-free prealignment provides an effective tool for controlling molecular deflection. Depending on the polarization of prealignment pulse, different control actions may be exerted. In particular, the deflection process may be turned off when the prealignment pulse is parallel to the direction of the deflecting field. Furthermore, we predict a dramatic increase in the brightness of the scattered molecular beam. Though we discussed (for simplicity) linear molecules in this work, a similar control mechanism may be considered for polyatomic molecules with more complicated geometry. Being in free space, such molecules rotate about their symmetry axis as well, which leads to \( A_2 \) distribution different from that of Eq. (7), and \( A_1 \) is not necessarily 0. For such molecules the prealignment will play a significant role in reducing their dipole interaction with the static field. Molecular deflection by inhomogeneous static electric fields may be used for the separation of molecular mixtures. 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,\textsuperscript{35} or nuclear spin isomers.\textsuperscript{36, 37} Controlling molecular deflection by means of laser-induced prealignment may be implemented also for magnetic molecules moving in the static inhomogeneous magnetic fields, and this phenomenon is a subject of the currently ongoing research. Controlling the dipole interaction by laser-induced prealignment may find applications in molecular deceleration methods using time and spatially varying electric and magnetic fields.\textsuperscript{38}

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APPENDIX: CALCULATION OF \( \mathcal{A}_{1,2} \) BY MEANS OF THE THEORY OF ADIABATIC INVARIANTS

The energy of a molecule participating in the deflection process is

\[
\mathcal{H} = \frac{1}{2} I \left( \dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta \right) - \mu \mathcal{E} \cos \theta,
\]  

(A1)

where we neglected the effect of polarizability (which is small for the fields and molecules considered in the main body of the paper). The conjugate momenta \( P_\theta \) and \( P_\phi \) are given by Eqs. (14) and (15), respectively, and \( P_\phi \) is a constant of motion. It is convenient to change variables and to define new constants:\textsuperscript{39, 40}

\[
u \equiv -\cos \theta, \quad \beta \equiv \frac{2}{I} \mathcal{H}, \quad \alpha \equiv \frac{2 \mu \mathcal{E}}{I}.
\]  

(A2) \hspace{1cm} (A3) \hspace{1cm} (A4)

It is easy to show that \( u \) obeys the following equation:

\[
\left( \frac{du}{dt} \right)^2 = (\beta - \alpha u)(1 - u^2) - \left( \frac{P_\phi}{I} \right)^2,
\]  

(A5)

which gives

\[
\frac{dt}{u} = \frac{du}{\sqrt{g(u)}},
\]  

(A6)

where \( g(u) \) is the rhs of the Eq. (A5). If \( \alpha = 0 \), the polynomial \( g(u) \) has two roots, \( u_1, u_2 \) such that \(-1 \leq u_1 \leq u_2 \leq 1 \). When \( \alpha \neq 0 \), \( g(u) \) has three roots (denoted by \( u_{1,2,3} \)). Let us analyze the behavior of this polynomial. If \( u \gg 1 \), then \( g(u) \approx \alpha u^3 > 0 \). If we substitute \( u = 1 \), then \( g(1) = - \left( \frac{P_\phi}{I} \right)^2 \leq 0 \). That means that the three real roots of \( g(u) \) are ordered as \(-1 \leq u_1 \leq u_2 \leq 1 \). The polynomial \( g(u) \) is positive between \( u_1 \) and \( u_2 \), and each root corresponds to a real angle \( \theta \). This allows one to determine the half-period of the motion in the static field \( \mathcal{E} \) by integrating Eq. (A6) from \( u_1 \) to \( u_2 \).

Since the potential is time-dependent (at least during the rising time), the energy of the system is not a constant of motion. However, the deflection potential is adiabatic with respect to the rotational motion and, therefore, we can use adiabatic invariants to determine the energy of the system.\textsuperscript{39–41}
The adiabatic invariant related to the coordinate $\theta$ is

$$I_0 = \int_{u_1}^{u_2} P_0 d\theta. \quad (A7)$$

From Eqs. (15), (A5), and (A7) it is easy to derive

$$I_0 = \kappa \int_{u_1}^{u_2} \frac{\sqrt{g(u)}}{1 - u^2} du, \quad (A8)$$

where $\kappa$ is a constant. The energy $\mathcal{H}$ of the molecule as a function of the energy $\mathcal{H}_0$ without electric field is obtained numerically by solving the following equation:

$$I_0 = I_0^0, \quad (A9)$$

where $I_0^0$ is calculated for $\alpha = 0$, that is in the absence of the external field.

Once the energy of the system $\mathcal{H}$ and the polynomial $g(u)$ are found, $A_{1.2}$ is given by

$$A_{1.2} = \frac{\int_{u_1}^{u_2} (-u)^{1/2} du / \sqrt{g(u)}}{\int_{u_1}^{u_2} du / \sqrt{g(u)}}. \quad (A10)$$

This is equivalent to calculating $A_{1.2}$ with the help of Eq. (19).

27. G. Tikhonov, K. Wong, V. Kasperovich, and V. V. Kresin, Rev. Sci. Instrum. 73, 1204 (2002).