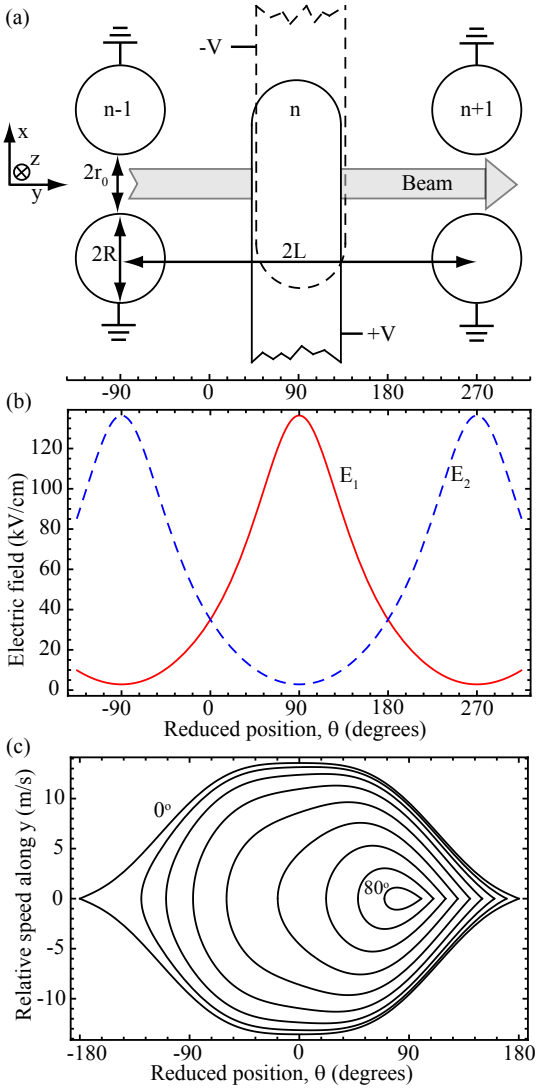

FIG. 1: (Color online) (a) Structure of the Stark decelerator, showing three consecutive deceleration stages centred on the n'th stage. Each stage is formed from a pair of rods whose axes are parallel to the z-axis for the odd-numbered stages, and to the x-axis for the even-numbered stages (n is even). For clarity, the two rods forming the n'th stage are shown slightly displaced, though in reality one should be exactly behind the other. (b) Electric field profile versus reduced position for the two switch configurations when $R = 1.5\,\mathrm{mm}$, $r_0 = 1\,\mathrm{mm}$, $L = 6\,\mathrm{mm}$, $V = 15\,\mathrm{kV}$. (c) Longitudinal phase-space acceptance for synchronous phase angles of 0° (outermost line), through to 80° (innermost line), in steps of 10°. The plot is for CaF molecules in the $|4,0\rangle$ state and for the electric field profile shown in (b).

decelerated. Note that these low-field seeking states all turn over to become high-field seekers when the field is large, and that the turning point shifts to higher electric field for larger values of $\mathcal{N}$ and B.

At time $t = 0$ the molecule is in the particular eigenstate $|\mathcal{N}_p, M_p\rangle_{E_1}$. We can calculate the time evolution of the state vector $|\alpha\rangle$ in the z-fixed basis $|NM\rangle$,

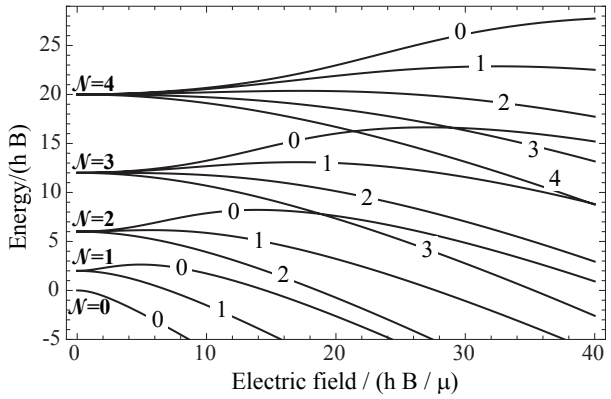

FIG. 2: Stark shift of the low-lying states of a rigid rotor molecule. States are labelled by their values of $\mathcal{N}$ and M.

by solving the Schrödinger equation for the coefficients $c_{NM} = \langle NM|\alpha\rangle$,

$$i\hbar\frac{d}{dt}c_{NM} = \sum_{N'M'}\langle NM|\hat{H}(t)|N'M'\rangle c_{N'M'}, \qquad (2)$$

with this initial condition and with $\hat{H}(t)$ given by Eq. (1). Having found the time evolution of $|\alpha\rangle$, we can then calculate the probability of finding the molecule in any one of the states $|\mathcal{N}, M\rangle_{E(t)}$ as a function of t.

Although this calculation is straightforward, the integration of Eq. (2) is slow because the basis set needs to include a large number of N states and because the timescale of the switch is vastly larger than $1/B$, which sets the scale for the time step in the integration. Fortunately, a few simple transformations provide us with an equation that is much faster to solve and which also makes it obvious that it is the rotation of the electric field vector that drives the transitions.

If the coordinate system were rotated so that the field at time t pointed along the local z'-axis, the instantaneous Hamiltonian would be $\hat{H}' = hB\hat{\boldsymbol{N}}^2 - \mu E(t)\hat{C}_0^{(1)}$, $E(t)$ being the electric field magnitude at time t. Hamiltonian (1) is related to this one by a rotation about the y-axis through an angle $\beta(t)$, $\hat{H} = \hat{D}^{-1}\hat{H}'\hat{D}$. Here $\hat{D}$ is the relevant rotation operator, $\hat{D} = \exp(-i\hat{N}_y\beta/\hbar)$. The evolution of the state vector $|\alpha\rangle$ is governed by the Schrödinger equation: $i\hbar\frac{\partial}{\partial t}|\alpha\rangle = \hat{H}(t)|\alpha\rangle$. Applying the rotation operator to both sides of this equation, and introducing the state vector in the rotating frame, $|\alpha'\rangle = \hat{D}|\alpha\rangle$, we obtain

$$i\hbar\,\hat{D}\frac{\partial}{\partial t}(\hat{D}^{-1}|\alpha'\rangle) = \hat{D}\hat{H}|\alpha\rangle = \hat{D}\hat{D}^{-1}\hat{H}'\hat{D}|\alpha\rangle = \hat{H}'|\alpha'\rangle. \qquad (3)$$

Using

$$\frac{\partial\hat{D}^{-1}}{\partial t} = \frac{i}{\hbar}\hat{N}_y\frac{d\beta}{dt}\hat{D}^{-1}, \qquad (4)$$

and the fact that $\hat{D}^{-1}$ commutes with $\hat{N}_y$, we obtain the