Cold dilute molecular systems are rapidly emerging as a front-line area at the interface of quantum optics and condensed matter physics [1]. An increasing subset of this activity centers around the creation of cold dilute gases of molecules possessing electric dipole moments. These in particular, owing to their long-range anisotropic interaction, hold the promise of novel physics, where two- and many-body quantum properties can be systematically studied. Cold dilute gases of dipolar molecules can be produced by forging a tight bond between two chemically distinct species of laser-cooled atoms, e.g., RbCs [2]. Alternatively, cold dilute gas ensembles can be created by buffer-gas loading [3] or electric-field manipulation of naturally occurring molecules like ND$_2$ [4,5] and H$_2$CO [6], metastables like CO [7], or radicals like YbF [8], OH [9], and NH [10]. So far all the cold molecules made available with electric-field-based methods have a Stark effect (in their relevant states) which is predominantly linear in the important range up to 150 kV/cm.

Here we report the creation of a slow beam of heavy-water (D$_2$O) molecules, which experience a quadratic Stark effect. The cold D$_2$O molecules are filtered from a room-temperature thermal gas [6] and have a translational temperature around 1 K. Because the Stark shifts are quadratic in the electric field, it follows that forces exerted by inhomogeneous electric fields are relatively small for D$_2$O compared to molecules with similar dipole moments but with linear Stark shifts. It is therefore by no means obvious that significant quantities of slow D$_2$O molecules can be produced by means of electric-field-based methods. Our experimental result therefore underlines the versatility of the velocity-filtering method. It is an enabling step toward future trapping of molecules for which the ratio of elastic to inelastic collisions is expected to be more favorable than for molecules with linear Stark shifts [11]. An additional advantage of the quadratically Stark-shifted molecules like D$_2$O is the possibility to perform precise spectroscopic measurements insensitive to stray electric fields, to the first order. Moreover, water is abundant in interstellar space at low densities and temperatures from a few kelvin upward, playing an important role in the chemistry of molecular clouds [12]. The conditions in these clouds are remarkably close to those achieved in our experiment, opening up the possibility to investigate in the laboratory chemical reactions under conditions found in space.

This Rapid Communication is structured as follows. First we discuss general features of Stark shifts of molecular states with particular reference to D$_2$O. We then present our experimental work with D$_2$O. This is followed by arguing from first principles that the resulting beam of D$_2$O is dominated by only four rotational states, despite starting with a thermal source of molecules at 300 K.

Several techniques have recently been developed to manipulate molecules [1] with electric fields. All of these exploit the Stark effect to exert a force on the molecules. In contrast to atoms, molecules can have a permanent electric dipole moment. Such molecules have much larger Stark shifts than nonpolar molecules. However, as described below, a large dipole moment alone is not enough to have a strong Stark effect. The direction and magnitude of the force exerted on the molecule in an inhomogeneous electric field depend on the details of the molecular rotational state. Assuming the Stark shift to be a monotonic function of the electric field, the molecule can be in either low-field-seeking (LFS) or high-field-seeking states, depending on the sign of the Stark shift.

The condition for having a linear Stark effect is that the component of the dipole moment $\vec{d}$ along a space-fixed direction, we can choose $\vec{z}$, is nonvanishing [i.e. $\langle \vec{d} \cdot \vec{z} \rangle \neq 0$]. Strictly speaking this requires a finite electric field, but it can be arbitrarily low. The linear Stark shift is typically found in symmetric-top molecules and is proportional to $|\vec{d}|K_M$, with $K$ and $M$ representing the projection of the total angular momentum $\vec{J}$ on the molecular symmetry axis and on the $z$ axis, respectively. Of course, no first-order Stark effect occurs if either $M$ or $K$—or both—is zero. If the degeneracy in zero field is lifted, e.g., by fine-structure splitting, inversion doubling, nuclear quadrupole interaction in a symmetric-top molecule, or $\Lambda$ doubling in linear molecules, the Stark splitting will no longer be linear in the limit of zero field. How-
The Stark shifts are obtained by numerically diagonalizing the Stark Hamiltonian ($J=0, \ldots, 12$), following Ref. [13], however, often those interactions are small enough as to lead to a nearly linear Stark splitting in the applied electric-field range.

In general, the linear Stark effect condition $(\vec{d} \cdot \vec{z}) \neq 0$ is not satisfied in asymmetric-top molecules. Under certain conditions, however, polar asymmetric molecules can also exhibit (nearly) linear Stark shifts. If the asymmetry is weak, the states that correspond to $K \neq 0$ in the prolate- or oblate-top limit will always be close to being degenerate. Those states show nearly linear Stark shifts if they are coupled by the Stark interaction. This is the case if the dipole is along the $a$ axis in the prolate limit, or along the $c$ axis in the oblate limit, where we follow the convention to label the axis with the smallest moment of inertia and hence the largest rotational constant with $a$, the intermediate axis $b$, and the axis with the largest moment of inertia $c$. An example is the nearly symmetric- (prolate-top) molecule $\text{H}_2\text{CO}$.

True asymmetric-top molecules in general have quadratic Stark shifts. Exceptions can occur for some states, if the dipole is oriented along the axis of largest or smallest moment of inertia. For molecules with their dipole oriented along the $b$ axis, we found no exceptions: all rotational states have a nonlinear Stark shift. Water, both $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$, presents such a case and a few levels of $\text{D}_2\text{O}$ are depicted in Fig. 1. The quadratic behavior is obvious: only for the highest most abundant states the $|J=3, \tau, M\rangle$ states (where $\tau$ is a pseudo quantum number labeling the state), is a deviation found. Moreover, the large rotational constants [14] for $\text{D}_2\text{O}$, $A=15.394$ cm$^{-1}$, $B=7.2630$ cm$^{-1}$, $C=4.8520$ cm$^{-1}$, imply large rotational level spacings. Avoided level crossings are neither expected nor found, and second-order perturbation theory is a reasonable approximation for the Stark shift computation of $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$. Moreover, since the contribution to the perturbation from each coupled pair of states is inversely proportional to the energy gap between the pair, the shift will be proportional to the density of (rotational) states, and therefore very small for the sparse rotational spectrum of $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$. Our choice of working with $\text{D}_2\text{O}$ as opposed to $\text{H}_2\text{O}$ has partly to do with the larger Stark shifts of $\text{D}_2\text{O}$ because of its smaller rotational constants. The treatment of the general case of an asymmetric molecule, where the dipole is not necessarily along one of the principal axes, is, of course, more involved.

Our apparatus [4] is depicted in Fig. 2. It consists of a room-temperature effusive thermal source, which injects $\text{D}_2\text{O}$ molecules directly between four 50-cm-long electrodes set up in a quadrupole arrangement, with neighboring electrodes having opposite polarities. The guide has two 90° bends with a radius of curvature of 25 mm. The quadrupolar electric field defines a two-dimensional potential well. This well has a depth that depends on the internal molecular state, e.g., for the $|J, \tau, M\rangle=|1, 1, 1\rangle$ state with a positive Stark shift of $0.20$ cm$^{-1}$ at $100$ kV/cm, the depth amounts to $0.29$ K. Molecules with transverse kinetic energy exceeding the potential depth escape the guide. In the bends the longitudinally fast molecules escape while the slow ones are kept due to the action of the centripetal force. These are guided through two differential pumping regions into an ultrahigh vacuum chamber for mass-spectrometric detection at the end of the electrodes. Heavy water is convenient for this purpose, as the background at its mass is virtually zero. The longitudinal velocity distribution of the guided $\text{D}_2\text{O}$ beam was determined by a time-of-flight method [6] at an escape field $E$ of $115$ kV/cm. We found a most-probable velocity of $24$ m/s in the laboratory frame, corresponding to a longitudinal temperature of $\approx 1.4$ K. The transverse temperature is expected to be on the order of $0.1$ K, as the guide presents a smaller transverse velocity cutoff value than the corresponding longitudinal velocity cutoff.

The flux dependence on the escape field $E$ and hence on the applied electrode voltage $V$ is characteristic of the nature of the guided molecules’ Stark shift. This can be seen as follows. Let $x, y$ be directions orthogonal to and $z$ be parallel to the quadrupolar axis. Let $f_{v_{x,y,z}}$ be functions proportional to the flux crossing the planes of unit area perpendicular to the $x, y, z$ axes, respectively [15]. Then $f_{v_{x,y}} \propto \exp(-v_{x,y}^2/\alpha^2)$ is bidirectional and $f_{v_z} \propto v_z \exp(-v_z^2/\alpha^2)$ is unidirectional along the positive $z$ axis. Here, $\alpha=\sqrt{2k_BT/m}$, $k_B$ the Boltzmann constant, $T$ the temperature of the reservoir the beam originates from, and $m$ the molecular mass.

Hence the total guided flux $\Phi \approx \int_0^{v_{x,y,z,\text{max}}} dv_x \int_0^{v_{x,y,z,\text{max}}} dv_y \int_0^{v_{x,y,z,\text{max}}} dv_z f_{v_x} f_{v_y} f_{v_z}$, where $v_{x,y,z,\text{max}}$ are the maximal guided velocities in each direction. As $\alpha \gg v_{x,y,z,\text{max}}$, $\Phi \propto v_{x,\text{max}} v_{y,\text{max}} v_{z,\text{max}}^2$. The maximum kinetic energy $U_{z,\text{max}}$ is given by the escape energy of the guide, i.e., the Stark shift in $E$, which is proportional to the applied electrode voltage $V$. Hence for molecules with a lin-

FIG. 1. The lowest rotational energies of $\text{D}_2\text{O}$ as a function of the applied electric field $E$. The five most abundant states $|J, \tau, M\rangle$ in the guided beam are indicated. The Stark shifts are obtained by numerically diagonalizing the Stark Hamiltonian ($J=0, \ldots, 12$), following Ref. [13].

FIG. 2. (Color online) Schematic of the experiment. On the left is the effusive source, which injects thermal $\text{D}_2\text{O}$ molecules into the four-wire guide. Neighboring electrodes have opposite polarity, creating a quadrupolar electric field. Molecules that are slow enough are guided through the first and second (not shown) 90° bends and are finally detected by a mass spectrometer.
neal Stark shift, \( \Phi \propto U_0^2 \propto V^2 \). For molecules with a quadratic Stark shift, \( U_0 \propto V^2 \), and hence \( \Phi \propto U_0^2 \propto V^4 \).

Our detector, a quadrupole mass spectrometer, converts molecules to ions by electron-impact ionization. The ions are then mass selected. Measurement on various molecules with a linear Stark shift indicate that the signal is to a good approximation proportional to the guided flux \([4,6]\). Scaling (for detector counting efficiencies, angular divergence of the beam exiting the guide) and corrections (velocity-dependent detection, branching ratios of ionization) are needed to convert our measured count rates (plotted in Fig. 3) to the absolute flux \( 7 \times 10^3 \text{s}^{-1} \) at \( V = 7 \text{kV} \), corresponding to an electric field depth of the guide of \( E = 134 \text{ kV/cm} \). The error bar of the flux is estimated to be of the order of a factor 2. The quartic dependence on \( E \) is clearly visible in Fig. 3 and proves the quadratic Stark shift of the guided molecules. Indeed, with the same apparatus it has been observed \([4,6]\) that for \( \text{H}_2\text{CO} \) and \( \text{ND}_3 \) (linear Stark molecules), the flux depends quadratically on \( V \).

As our slow beam originates from a room-temperature source, many rotational states are populated. This is illustrated in Fig. 4, where the Stark shifts of \( \text{D}_2\text{O} \) in a field of 100 kV/cm have been plotted as a function of the zero-field rotational energy. The Stark shifts are obtained by numerically diagonalizing the Stark Hamiltonian for a rigid asymmetric rotor, following the procedure of Ref. \([13]\). It is known that the rigid-rotor assumption is only a coarse approximation when estimating the absolute energies of \( \text{D}_2\text{O} \) states. In the present case, however, the approximation is expected to be good if one is only interested in the Stark shifts and not in the absolute energies, because the Stark shifts are caused by the coupling of adjacent states that do not differ much in their sets of rotational quantum numbers, leading to relatively small sensitivity to the centrifugal distortion. We have also neglected hyperfine couplings, which is completely justified in the range of field strengths used in our experiments. As input for the Stark shift calculations we took the rotational constants and the dipole moment \( \mu = 1.87 \text{ D} \), which is directed along the \( b \) axis \([14]\). Note that as a general trend, the Stark shifts decrease with rotational energy.

As discussed earlier the room-temperature rotational spectrum of \( \text{D}_2\text{O} \) is very sparse. The populations in the thermal gas in the effusive source can be estimated by weighting all thermally populated states with the Boltzmann factor, their orientational \( (M) \) degeneracy and the spin-statistical weight \([16]\). Further, only very few of these levels have large enough Stark shifts to be guided. This selection is much more pronounced for molecules with a quadratic Stark shift than for molecules with a linear Stark shift. The intuitive reason is that for molecules with a quadratic Stark shift, the electric field must first orient the dipole in space, which is harder for faster rotating molecules. Indeed, for these molecules the Stark shift \([14]\) is approximately proportional to \( 1/(J+1) \). Hence, the (maximum) Stark shifts decreases with \( J \), as can be seen for \( \text{D}_2\text{O} \) in Fig. 4. This should be compared with the dependence of the Stark shift on \( J \) of molecules with a linear Stark shift. For the generic example of a symmetric top, this shift is proportional to \( [\hat{d} K ME]/[J (J+1)] \) \([14]\). As \( (K, M) \in \{−J, \ldots, 0, \ldots J\} \), the Stark shift of the maximum \( (K, M) \) for molecules with a linear Stark shift will not decrease with \( J \). In fact, knowing that the flux of \( \text{D}_2\text{O} \) molecules is proportional to the square of the Stark shift, and assuming that this dependence holds for each state, the four most populated states contribute more than 70% of our guided flux. The partial contributions, zero-field energy, and Stark shifts of the five most abundant states are summarized in Table I. One should note that the beam purity \([17]\) is independent of voltage changes as long as all the states are

![FIG. 3. Detector signal versus the electrode voltage \( V \). The data follow a quartic law in \( V \), as illustrated by the \( V^4 \) fit (solid line). The dotted line shows a \( V^2 \) fit attempt.](image)

![FIG. 4. Stark shifts \( \Delta W_3 \) in an electric field of 100 kV/cm of LFS rotational states of \( \text{D}_2\text{O} \) in its vibrational and electronic ground state, as a function of the zero-field rotational energy \( E_{rot} \). The inset shows the Boltzmann factor at \( T=300 \text{ K} \). The five most Stark-shifted states are labeled \( J, \tau, M \). Note that the spin-statistical weighting is not shown.](image)

<table>
<thead>
<tr>
<th>State</th>
<th>Contribution (%)</th>
<th>( E_{rot} ) (cm(^{-1}))</th>
<th>( \Delta W_3 ) (cm(^{-1}))</th>
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<td>(</td>
<td>3,−2,1</td>
<td>)</td>
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<td>3,−2,0</td>
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quadratic in nature.

In conclusion, we have demonstrated the effective Stark manipulation of a polar molecule with quadratic Stark shifts over the range of applied fields of 0–135 kV/cm. This experimentally shows the feasibility of the velocity-filtering method for quadratically Stark-shifted molecular states. Using this method we have created water vapor (D₂O) at a translational temperature of ≈1 K. Its quadratic Stark effect combined with a large rotational spacing make D₂O a promising molecule for electric trapping [18] and even evaporative cooling.

We acknowledge financial support by the Deutsche Forschungsgemeinschaft (SPP 1116).

[17] Note that the guided beam is not in internal equilibrium. The average rotational energy of the beam corresponds to that of a thermal gas of 81 K. The purity, however, is equivalent to that of a thermal gas of 23 K, as calculated from the entropy of the internal distribution.