Stark-selected beam of ground-state OCS molecules
characterized by revivals of impulsive alignment

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We make use of an inhomogeneous electrostatic dipole field to impart a quantum-state-dependent
deflection to a pulsed beam of OCS molecules, and show that those molecules residing in the absolute
ground state, \(X^1\Sigma^+, |00^00\rangle, J = 0\), can be separated out by selecting the most deflected part of the
molecular beam. Past the deflector, we irradiate the molecular beam by a linearly polarized pulsed
nonresonant laser beam that impulsively aligns the OCS molecules. Their alignment, monitored via
velocity-map imaging, is measured as a function of time, and the time dependence of the alignment
is used to determine the quantum state composition of the beam. We find significant enhancements
of the alignment (\(\langle \cos^2 \theta_{2D} \rangle = 0.84\)) and of state purity (\(> 92\%\)) for a state-selected, deflected beam
compared with an undeflected beam.

The ability to produce ensembles of atoms and molecules
with a narrow distribution of quantum states has been a
game-changer in atomic, molecular and optical physics,
past and present. Recent examples from molecular
physics include crossed beam scattering [1–4] and pho-
todissociation dynamics studies at high resolution [5], as
well as the work done with and on cold and ultracold
molecules [6, 7]. The techniques developed to produce
molecules in (nearly) single quantum states include mul-
tipole focusing [8–12], Stark deceleration [13, 14], Zeeman
deceleration [15, 16] – all of which isolate molecules that
are initially populated in a particular quantum state –
and buffer gas cooling [17, 18] – which lowers the tempera-
ture of a sample such that the resulting thermal state-
distribution contains essentially only the absolute ground
state. Alternatively, ultracold alkali atoms can be photo-
or magneto-associated and form ultracold homo- or het-
eronuclear diatomic molecules occupying a single elec-
tronic, vibrational and rotational state [19, 20] including,
in certain cases, the absolute ground state [21, 22]. All
methods offer unique opportunities but are also subjected
to limitations in terms of the type of molecules that the
methods apply to or the particular quantum states that
can be selected.

Here we demonstrate an alternative method, with a
history reaching back to the 1920s [23–25], to produce
molecules in a single quantum state. Like multipole fo-
cusing and Stark or Zeeman deceleration it is based on
selecting the molecules that are initially residing in a spe-
cific quantum state. We employ a dipolar deflection field
to disperse a well-expanded, nearly monoenergetic beam
of OCS molecules according to their state-specific elec-
dric dipole moments. The inhomogeneous electric field
inside the deflector has an almost constant gradient over
a large area surrounding the molecular beam axis and
enables dispersion of the rotational quantum states of
OCS. In particular, we separate out the ground rotational
state, \(J = 0\), of the electronic and vibrational ground
state, \(X^1\Sigma^+\) and \(|00^00\rangle\), and thereby produce a molec-
ular beam of OCS\( (X^1\Sigma^+, |00^00\rangle, J = 0) \) with a purity
in excess of 92%. Since \(^{16}\text{O}^{12}\text{C}^{32}\text{S}\) has zero nuclear spin,
the ground state obtained is free of hyperfine structure.
The purity of the beam was characterized by observing the
time dependence of the nonadiabatic alignment [26–
29] produced by the interaction of a linearly polarized
nonresonant pulsed laser beam with the anisotropic OCS
molecules.

In what follows, we first present an outline of the ex-
perimental setup. Then we describe the dispersion of the
molecular beam achieved by the dipole deflector. The
nonadiabatic alignment of the molecules and its use to
characterize state purity of the molecular beam is de-
scribed next. Finally, we draw conclusions from our work.

The experimental setup, detailed earlier [30, 31], is
shown in Figure 1. A pulsed molecular beam is produced
by expanding a mixture of 10 bar of Neon and 1 mbar
of OCS into vacuum through a 250 \(\mu\)m diameter nozzle
in a pulsed valve. The beam is collimated by a skimmer
and sent into a 15 cm-long electrostatic deflector, which
exerts a force on the molecules along the y-axis, cf. Fig-
ure 1. After the exit of the deflector the molecules travel
another 17 cm through a region between two parallel elec-
trostatic plates (field strength: 2 kV/cm) to preserve a
field-quantization axis before they enter into a velocity
non deflected:

\[
OCS + \text{Signal [arb.unit]}
\]

FIG. 1. Schematic of the experimental setup. The inset shows an S\(^+\) ion image recorded when the molecules are aligned along the y-axis \((t = 40.6\ \text{ps})\). The arrows indicate images of the S\(^+\) + CO\(^+\) Coulomb-explosion channel employed to determine the degree of alignment.

The effect of the deflector on the molecular beam was characterized by measuring the intensity profile of the molecular beam along the (vertical) y-axis, see Figure 2. This was done by recording the OCS\(^+\) signal, arising from the ionization of OCS by the probe pulse as a function of the vertical position of the laser focus, see Figure 1. When the deflector is turned off, the vertical width of the molecular beam is about 2.2 mm, mainly due to the collimation of the beam by the skimmers, which precede the deflector. When the deflector is turned on, the molecular beam profile broadens and shifts upwards, toward higher field strengths (corresponding to higher values of \(y\)). The molecular beam profiles were modeled by a Monte-Carlo simulation. For every relevant eigenstate of the initial OCS packet we generated a test sample of initial values of molecules in phase-space \((x, y, z, v_x, v_y, v_z)\) and then performed (classical) trajectory simulations through the inhomogeneous electric field of the deflector. This yields a vertical beam profile for the given molecular quantum state. These profiles for individual states were averaged with a weight according to their populations – according to a Boltzmann distribution for different rotational temperatures \(T\) of the beam and their degeneracy. In Figure 2 (a) the resulting profiles for 0.2 K, 0.4 K, and 0.6 K are given along with the experimental curve. A comparison of the measured and simulated data indicates that the \(T = 0.4\ \text{K}\) curve represents the experimental data best. However, a non-negligible discrepancy remains, particularly on the left tail of the deflection profile, corresponding to negative values of \(y\). Likely culprits are potential increases of the low-field seeking \(|10\rangle\) and \(|20\rangle\) states (with theoretical populations at \(T = 0.4\ \text{K}\) of 13% and 1.2%, respectively). This is illustrated in Figure 2(b), which shows the Boltzmann-weighted profiles of the individual Stark states at \(T = 0.4\ \text{K}\). An excess of the \(|10\rangle\), \(|20\rangle\) states is consistent with the experimental observations made for the impulsive alignment of
OCS, described below. For the case of the temperature-independent direct (non-deflected) beam, the simulations reproduce the experimental data accurately.

Figure 2(b) further shows that of the upward-deflected high-field-seeking states, the |00⟩ state deflects the most, followed by the |11⟩ state, and the |22⟩ state; the low-field-seeking |10⟩ state deflects downwards. At y = 1.5 mm, 89% of the molecules are in the |00⟩ state and 11% in the |11⟩ state, while the population of the |22⟩ state is negligible.

In order to characterize the quantum state composition of the deflected molecular beam, we conducted a nonadiabatic alignment experiment: At time t = 0, the molecular beam is irradiated by an alignment pulse, see Figure 1. The peak intensity of 9.6 × 10^{12} W/cm² is low enough to preclude any detectable ionization of OCS. Within its focal volume, the alignment laser pulse nonadiabatically excites each molecule to a nonstationary, rotational wave packet, which undergoes periodic revivals, as does the concomitant alignment. The rotational wave packet dynamics is probed by irradiating the molecules with a probe pulse (I_{probe} = 4.8 × 10^{14} W/cm²) at a time t. The probe pulse double-ionizes some of the OCS molecules, triggering their Coulomb explosion into CO⁺ and S⁺ ion pairs. This particular fragmentation channel can be identified by the recoil velocity as a pair of radially displaced half-rings in the outermost region of the S⁺ ion images, such as those shown in the inset of Figure 1.

In keeping with our previous work, we assume that the Coulomb explosion occurs rapidly enough for the axial recoil approximation to apply, in which case the emission direction of the ions is straightforwardly related to the alignment of the molecule at the instant of ionization. We quantify the alignment attained by the (experimental) degree of alignment, ⟨cos²θ_{2D}⟩, where θ_{2D} is the angle between the velocity vector of the S⁺ ion in the detector plane and the polarization plane of the alignment laser pulse.

Figure 3 displays the rotational wave packet dynamics, represented by the dependence of the alignment degree ⟨cos²θ_{2D}⟩ on time over the intervals −2 ps < t < 52 ps and 77 ps < t < 89 ps. The two blue traces pertain to undeflected (deflector off) and the red trace to the deflected (deflector on) molecules for the laser foci placed at y = 1.5 mm, cf. Figure 2(b). The most prominent features of the undeflected-beam trace are the prompt alignment arising shortly after the arrival (and passing) of the alignment pulse near t = 0, the half-period revival centered at t = 20.7 ps, and the first full-period revival centered at t = 39.6 ps.

In order to account for the observed alignment dynamics, we solved numerically the time-dependent Schrödinger equation for the interaction of a linearly polarized laser field with the anisotropic polarizability of the OCS molecule [26, 32], and evaluated the state-specific expectation values of the alignment cosine, ⟨cos²θ⟩_{JM}, for each initial rotational state, |JM⟩, of 16O^{18}C=OS. The time dependence of the alignment cosine for the |00⟩, |11⟩, and |22⟩ states is shown in Figure 4(a)-(c). While the revival structures of the alignment cosines for the three states are similar and in phase at the half- and full-period, the revival structures at the quarter- and three-quarter-period are out of phase with respect to one another for states with opposite parity, (−1)^J, i.e., the even-parity |00⟩ and |22⟩ states on the one hand and the odd-parity |11⟩ state on the other. Panel (d) of Figure 4 shows the ensemble average, ⟨⟨cos²θ⟩⟩ = Σ_J w_JΣ_M⟨cos²θ⟩_{JM}, of the alignment cosine [34], with w_J the Boltzmann weights of the initial rotational states (these are w_0 = 0.567; w_1 = 0.396; w_2 = 0.036 at T = 0.4 K). The time dependence of ⟨⟨cos²θ⟩⟩ exhibits the same revival structure as the experimental dependence for the undeflected beam, blue squares in Figure 3. In particular, the quarter- and three-quarter period revivals are almost absent, due to the destructive interference of the opposite-parity contributions to ⟨⟨cos²θ⟩⟩ from the initial rotational states |00⟩ and |10⟩.

For the deflected beam (red circles in Figure 3), the revival structure strikingly differs from that of the undeflected beam: Firstly, a prominent quarter-period revival is now present. As Figure 4(a)-(c) indicate, this can only come about if most of the beam molecules have the same parity. Since the position of the local minimum of the observed quarter revival (at 20.9 ps) matches that due to the |00⟩ and the |22⟩ states (at 20.7 ps), but not due to the |11⟩ state (at 19.7 ps), it must be the |11⟩ state whose concentration in the beam has been diminished. The skewed structure with a local maximum (at 18.9 ps) followed by a local minimum (at 20.9 ps) and then another (slightly lower) local maximum (at 21.7 ps) fits the simulated |00⟩ trace well but is at odds with the simulated |22⟩ trace. Similarly, the shapes of the observed
half- and full-period revivals resemble closely those calculated for the |00⟩ but not for the |22⟩ state. These observations corroborate what the simulated deflection curves, Figure 2, have suggested, namely that the molecular beam (at y = 1.5 mm) is dominated by the |00⟩ state.

A quantitative assessment of the fraction of the |11⟩ state in the deflected beam could be obtained by comparing the amplitude of the (left) local maximum at the quarter-period revival (at 18.9 ps) to the prompt alignment maximum (at 0.9 ps). This is because, as seen in Figure 4(b) and (c), molecules in the |00⟩ or |11⟩ states cause the local maximum to rise or drop, respectively, in comparison with the prompt-alignment maximum. In this way, we found that at least 92% of all the beam molecules must be in the |00⟩ state to account for the observed revival amplitudes, Figure 3. The deflection curves suggest 89% population of the |00⟩, in fair agreement with the alignment revival data. We note that we do not expect the simulated deflection curves to identify the y position of the molecular profile to an accuracy better than 0.1 mm. This has repercussions for our ability to quantify the populations of the states. For instance, at y = 1.6 mm the simulations yield a 94% population of the |00⟩ state.

Our assessment of the populations of the rotational states in the beam was corroborated by yet another piece of evidence: in the absence of the alignment pulse the measured alignment degree for the undeflected beam is ⟨cos² θ⟩ = 0.50, as it should for an isotropic ensemble, cf. ⟨cos² θ⟩ in Figure 3 just before the alignment pulse (t = −1 ps)). For the deflected beam, the measured alignment degree has still the isotropic value of 0.50 or perhaps marginally smaller. This is only possible if essentially only the isotropic ground state |00⟩ with ⟨cos² θ⟩ = 0.5 is present in the deflected beam while the anisotropic states |11⟩ and |22⟩ with ⟨cos² θ⟩ = 0.375 and 0.312, respectively, are nearly absent.

Secondly, the alignment trace in Figure 3 pertaining to the deflected beam exhibits a significantly more pronounced modulation of the half- and full-period revivals than the trace for the undeflected beam. Inspection of the half-period revival reveals that the local maximum of ⟨cos² θ⟩, which is also the global maximum, is increased from 0.77 for the undeflected beam to 0.84 for the deflected beam. We note that we did not measure the 3/4-period revival but, according to our calculations, its local alignment maximum is well below that obtained at the 1/2-period revival. Likewise, the global minimum of ⟨cos² θ⟩ attained at the full-period revival (t = 81.6 ps, see Figure 3) decreases from 0.39 to 0.33. This means that not only alignment but also anti-alignment, i.e. confinement of the molecular axis to the plane perpendicular to the polarization vector of the alignment pulse, is significantly enhanced by using the deflected, state-selected beam compared with the direct beam.

The calculations displayed in Figure 4 predict that the alignment cosine, ⟨cos² θ⟩, only increases from 0.86 for a 0.4 K thermal ensemble to 0.87 for a pure |00⟩ state. Even for a 1 K beam, the alignment cosine is 0.85. Therefore, the much more pronounced enhancement of the alignment observed experimentally is likely due to a rotational state distribution in the direct beam which is not strictly Boltzmannian. As noted above, the measured deflection curves, Figure 2, indicate that the direct beam contains an excess of molecules in the |10⟩ and possibly also the |20⟩ states. Our calculations show that the alignment of these states at the half-period revival is significantly less than the alignment of the |00⟩, |11⟩ and |22⟩ states. As a result, an increased concentration of the |10⟩ and the |20⟩ states in the molecular beam would lead to a weaker alignment than for a thermal beam with a Boltzmann distribution of rotational states; such non-Boltzmann behavior of supersonic expansions is a well-known phenomenon [35–38]. Overall, the deflector is well-suited for generating molecular beams that can be

FIG. 4. Panels (a)-(c) show time dependence of the alignment cosine, ⟨cos² θ⟩, of OCS calculated over a rotational period of the molecule for different initial rotational states |JM⟩. Panel (d) shows the time dependence of the ensemble-averaged alignment cosine ⟨⟨cos² θ⟩⟩ of OCS at a rotational temperature T = 0.4 K. Focal volume averaging was accounted for by including an I³ probe detection efficiency based on measurements of the intensity dependence of the ionization yield.
particularly strongly aligned.

Selecting out rotational-ground-state molecules by electrostatic deflection will be particularly effective for species with a small moment of inertia (large rotational constant), such as many diatomic and small polyatomic molecules. Supersonic molecular beams of such species tend to have a large population of the rotational ground state. The single-quantum-state selected beam may have then an intensity of up to tens of percent of the undeflected beam. Examples include IBr, ICN, ClCN, C$_2$F$_3$, and CH$_3$I. For larger (and heavier) polyatomics, the number of states populated increases rapidly with the moment of inertia and temperature, and thus selection of the rotational ground state, if at all feasible, will occur at the expense of a much reduced beam intensity.

The ability to select out the absolute ground state of molecules by the deflection method has implications for several research areas: (1) Laser-induced alignment will clearly benefit from a state selection by the deflector, as demonstrated here. So will orientation based on pure optical methods [39, 40] as well as on the combined electrostatic and nonresonant radiative fields [30, 31, 41–44]. In particular, related work relying on state-selection by an electrostatic hexapole has already demonstrated that single-state molecular beams are conducive to producing tightly aligned or oriented molecules [43, 44]. (2) Collision/reaction dynamics in crossed molecular beams. (3) Ground-state molecules selected out by the deflector could be efficiently optically decelerated and trapped [45], thus opening an alternate route to trapping for molecules which cannot be, for instance, Stark-decelerated.
