We demonstrate and analyze a strongly driven quantum pendulum in the angular motion of state-selected and laser-aligned OCS molecules. Raman-couplings during the rising edge of a 50-picosecond laser pulse create a wave packet of pendular states, which propagates in the confining potential formed by the polarizability interaction between the molecule and the laser field. This wave-packet dynamics manifests itself as pronounced oscillations in the degree of alignment with a laser-intensity dependent period.

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The probe pulses were compressed to 30 fs using the laser pulses [24]. The alignment pulses can be compressed or stretched spatially by using an external compressor continuously to pulse durations ranging from 40 fs to 520 ps. The probe pulses were compressed to 30 fs using the standard grating based compression setup. Since both beams were generated by the same laser system they were inherently synchronized. Both beams were incident on a 60 cm-focal-length lens, parallel to each other, with a transverse distance of 10 mm. The foci were overlapped in space and in the molecular beam in the center of the velocity-map-imaging spectrometer. The relative timing between the two pulses was adjusted by a motorized linear translation stage.

In our theoretical description, we solved the time-dependent Schrödinger equation [23] starting in the field-free rotational ground state and using the experimental temporal profile of the laser intensity. The angular part of the interaction potential between the molecules and the nonresonant laser field, \(-i(t) \Delta a \cos^2 \theta / (2\c\epsilon_0)\), is presented in Figure 2a for \(I = 6 \cdot 10^{11} \text{W/cm}^2\); \(I\) is the laser intensity, \(\Delta a\) the polarizability anisotropy, and \(\theta\) the angle between the alignment laser polarization, \(Y\), and the axis of the molecule, \(z\). Moreover, the energies of the pendular states \(\langle J, M \rangle\) in that potential are depicted. Here, the \(\langle J, M \rangle\) labels are used for the pendular states that correlate adiabatically with the field free rotational states \(|J, M\rangle\). To rationalize the experimental observations, we computed the degree of alignment \(\langle \cos^2 \theta_2 \rangle\) and the decomposition of the wave packet in terms of the adiabatic pendular eigenstates. Our theoretical description includes the velocity distribution of the ions after the Coulomb explosion and a volume effect model which takes into account the spatial intensity profiles of the alignment and the probe laser pulses [24].

Figure 3a shows the degree of alignment measured as a function of the delay between the alignment and probe laser pulses for an alignment pulse duration of 450 fs (impulsive alignment) and a peak intensity of 1.5 \(\cdot 10^{13} \text{W/cm}^2\). These results fully agree with previous experiments and the analysis of the prominent quarter-period revival confirms that the molecules are prepared in the absolute ground state \(J = 0\) [29].

Figure 3c shows the degree of alignment for a pulse duration of 485 ps and a peak intensity of 2.2 \(\cdot 10^{13} \text{W/cm}^2\). The temporal laser profile is indicated by the shaded area. The rise- and fall-times of the pulse are 100 ps and 150 ps, respectively (10%–90%). The degree of alignment adiabatically follows the temporal laser profile as expected for pulses where all relevant time scales are larger than the rotational period of the molecule.

Figure 3b shows the time dependence of the degree of alignment for a pulse duration of 50 ps (FWHM in intensity) and intensities 4.5 \(\cdot 10^{10} \text{W/cm}^2\) (blue), 7.5 \(\cdot 10^{10} \text{W/cm}^2\) (green) and 6 \(\cdot 10^{11} \text{W/cm}^2\) (red). The 10%–90% rise time of the laser pulse is 10 ps. It is followed by a plateau where the laser intensity is approximately constant. With \(\tau_{\text{rot}} \approx 82\) ps this places the temporal features of the pulse between adiabatic and impulsive alignment. The rising edge of the laser pulse creates a wave packet of pendular states through Raman-coupling with selection rules \(\Delta J = 0, \pm 2\) and \(\Delta M = 0\). This wave packet propagates in the effective potential
The oscillation frequency increases with increasing peak intensity of the alignment laser, indicating the admixing of higher-angular-momentum states. Simultaneously, the amplitude of the oscillations decreases, depicting the stronger angular confinement of the molecules deeper in the potential and, therefore, a smaller change in the degree of alignment. The oscillations are very pronounced at the beginning of the laser pulse, but their amplitude decreases toward the end of the pulse. Initially, the phase of oscillation is defined by the rising edge, i.e., it is nearly the same for all molecules. The decrease during the laser pulse is mainly attributed to the volume effect, i.e., different molecules experiencing different laser intensities. Additional contributions to the decrease of contrast in the amplitude of the oscillations are due to the not completely flat temporal laser-intensity profile and the anharmonic-oscillator potential.

The calculated decomposition of the wave packet in terms of its pendular-state basis for the 50 ps pulse of intensity $6 \cdot 10^{11} \text{ W/cm}^2$, shown in Figure 3b, is given in Figure 2b. The coefficients show rapid changes at the two edges of the pulse, whereas they keep an approximately constant value in the plateau region. Here, only $|0, 0>, |2, 0>,$ and $|4, 0>,$ contribute significantly to the dynamics. The oscillations in the degree of alignment are due to the temporal evolution of the phase of these pendular states. Figure 2a illustrates that during the pulse all contributing states are bound in the potential well. For the 4.5 $\cdot 10^{10} \text{ W/cm}^2$ and 7.5 $\cdot 10^{10} \text{ W/cm}^2$ pulses the pendular ground state has by far the largest contribution (≥ 0.89) to the wave packet. Thus, the oscillations in $\langle \cos^2 \theta_{2D} \rangle$ are due to the coherence between $|0, 0>$ and $|2, 0>$, with the latter being unbound for these intensities. These two-state interferences are reflected by the cosine-like oscillations of the degree of alignment.

To obtain further insight into the alignment dynamics in the intermediate regime the degree of alignment is

![Image of Figure 3](image3.png)

**FIG. 3.** Measured degree of alignment ($\langle \cos^2 \theta_{2D} \rangle$) as a function of the delay between the alignment and probe laser pulses for an alignment pulse duration of a) 450 fs, b) 50 ps and c) 485 ps. The temporal profiles of the alignment laser pulses are indicated by the gray areas.

![Image of Figure 4](image4.png)

**FIG. 4.** $\langle \cos^2 \theta_{2D} \rangle$ as a function of the delay between the alignment and the probe laser pulses and the peak intensity of the alignment laser pulse. The alignment pulse duration is 50 ps. a) Experimental, b) theoretical results.
recorded for a range of alignment pulse peak intensities as a function of time. The alignment pulse duration is 50 ps as in Figure 3a. A 2D representation of the experimental results is shown in Figure 4a. The corresponding theoretical calculations are shown in Figure 4b. The oscillatory behavior of the degree of alignment during the laser pulse (between 10 ps and 50 ps) is again strongly visible. The frequencies of the oscillations are small in the low intensity regime (vide supra). As the laser intensity is increased more and more oscillations are observed.

Figure 4 also shows a complex behavior of the degree of alignment as soon as the laser is switched off, with a strong dependence on the intensity of the laser pulse. At low laser intensities we observed a revival structure corresponding to a single-cosine dependence due to the beating of |0⟩ and |2⟩. Moreover, for an intensity of \(7.5 \times 10^{10} \text{ W/cm}^2\), we find that the revival structure is strongly suppressed and only a weak revival structure is observed; this is also visible in the green trace in Figure 3b. For these conditions, the field-free state after the laser pulse closely resembled the initial field-free state [15]. The phase between wave packet components is modified by the falling edge of the laser pulse in such a way that the revival structure is coherently switched off. This effect repeats itself for increasing laser intensities. These quantum interferences are similar to those previously observed with two appropriately delayed laser pulses [23]. The revival structure is strongly suppressed and only a weak revival structure is observed; this is also visible in the green trace in Figure 3b. For these conditions, the field-free state after the laser pulse closely resembled the initial field-free state [15]. The phase between wave packet components is modified by the falling edge of the laser pulse in such a way that the revival structure is coherently switched off. This effect repeats itself for increasing laser intensities. These quantum interferences are similar to those previously observed with two appropriately delayed laser pulses [23].

For \(I_{\text{max}} \approx 6 \times 10^{10} \text{ W/cm}^2\) these computations predict no alignment once the pulse is off with small oscillations around the mean value of \(\langle \cos^2 \theta_{25} \rangle \approx 0.50\). The incomplete suppression of the experimental alignment structure is attributed to the volume effect and, thus, the simultaneous observation of dynamics for different field-strengths.

In conclusion, we studied the time dependent alignment behavior of state-selected OCS molecules in their absolute ground state for a pulse duration in the intermediate regime, between impulsive and adiabatic alignment. We observed strong oscillations in the degree of alignment during the laser pulse. These oscillations are attributed to the propagation of a wave packet in the potential of the molecule in the alignment laser field. The observed motion is the quantum analogue of an oscillating pendulum. Our results show the opportunity to initiate and to stop wave packet motion within a short period and by a single laser pulse. It provides an effective coherent control scheme of molecular motion.

The wave packet dynamics inside the effective potential has implications on the performance of experiments with laser aligned molecules such as the investigation of molecular-frame photoelectron angular distributions [9], the detection of structural changes via X-ray and electron diffraction [6, 11, 25, 27] and photoelectron holography from within [10], because typically a strong degree of alignment is required for these experiments.

Reducing the jitter of the relative timing and applying the appropriate delay of the alignment and probe laser allows for the strongest degree of alignment to be achieved, since the molecules can be probed at one of the maxima of \(\langle \cos^2 \theta \rangle\) of the pendular state dynamics. This holds especially for large molecules with rotational periods on the order of a few nanoseconds (ns), where non adiabatic effects will start to play a role even with ns laser pulses that are often employed to strongly fix molecules in space.

The observed pendular motion has implications on the performance of ultrafast molecular switches based on internal-rotation dynamics [28, 29]. The torsional motion of non-rigid quantum objects [7, 30] or surface adsorbed molecules [28, 31, 32] is governed by a 2\(\pi\)-periodic potential about the torsional or dihedral angle [33]. Variations in the relative alignment of the two moieties will lead to variations in, e.g., the current through a molecular switch [30, 34]. Inducing a wave packet of the internal rotation to coherently switch the system and terminating the motion in the desired position by the end of the laser pulse [35, 37] would work even when the surrounding media is not dissipative.

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