

Synchronised molecular rotations for novel investigations.

Controlling the collective quantum motion of molecules

We demonstrate strong laser-field-free orientation of ground-state-selected carbonyl sulphide molecules *via* coherent superposition of its two lowest rotational states. The states were coupled by the combined action of a 485-ps-long non-resonant laser pulse and a weak static electric field. The observed wave packet motion exhibits strong transient molecular orientation after the control laser pulse has been switched off. The experimentally attained degree of orientation $\langle \cos \theta \rangle \approx 0.6$ corresponds to the theoretical maximum for mixing of the two states. Simulations show that switching off the static field would provide the same orientation completely field free.

Alignment and orientation of small molecules in the gas phase opens up new opportunities for molecular imaging and for studies of chemical dynamics. Applications range from stereo-chemistry [1] over imaging of molecular orbitals via measurements of photoelectron angular distributions in the molecular frame [2] or high-order harmonic generation [3] to electron [4] and X-ray diffraction [5]. Individual molecules do not produce strong enough diffraction signals when exposed to intense X-ray flashes from, e.g., free-electron

lasers — in contrast to molecules in crystals. It is, therefore, highly desirable to control the spatial orientation of isolated molecules in the gas phase, which allows for adding up signals from many individual samples. Furthermore, controlling the spatial orientation of the molecules leads to an enhancement of the information that can be retrieved from a diffraction pattern, such as bond angles. However, molecular-frame photoelectron-angular-distribution imaging of adiabatically oriented molecules can show unwanted streaking features due to the presence of the alignment-laser field.

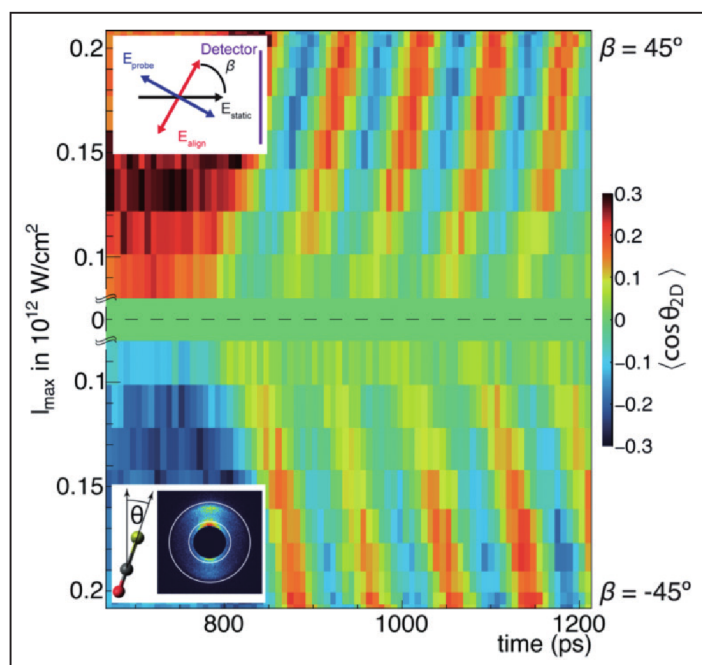


Figure 1

Experimental evolution of the degree of orientation as a function of the relative timing between the orientation laser pulse and the probe pulse and the peak intensity of the orientation laser for $\beta = 45^\circ$ (upper half) and $\beta = -45^\circ$ (lower half). β is defined as the angle between the DC static electric field and the polarisation axis of the orientation laser. θ is defined as the angle between the projected bond axis of the molecule and the vertical axis of the integrated detector image.

In our experiment, a pulsed molecular beam was provided by expanding 500 ppm of carbonyl sulphide (OCS) seeded in 6 bar of neon through a cantilever piezo valve, resulting in a rotational temperature of about one Kelvin. Using the electric deflector the molecules were dispersed in space according to their quantum state [6], and a pure sample of ground-state OCS was selected. These molecules were oriented by the combined action of a moderately intense, 485-ps-long, linearly polarised laser pulse ($I_{\text{control}} \approx 0.215 \text{ TW/cm}^2$) and a weak DC electric field ($E_{\text{stat}} = 840 \text{ V/cm}$) inside a velocity map imaging (VMI) spectrometer. The polarisation of the control laser was set to an angle of $\beta = \pm 45^\circ$ with respect to the static electric field. The spatial distribution of the molecules was probed using Coulomb explosion imaging following multiple-ionisation with a 30 fs laser pulse. The detected S^+ ion velocity distribution was highly directional and provided direct information on the orientation of the OCS molecules at the time of ionisation.

The coupling between the two rotor states is induced by the interaction with the mixed DC and AC electric field. As the control laser field is switched on, the almost free molecular rotor transforms into so-called pendular states, eigenstates of the complete Hamiltonian of the molecule in the field, which librate about the polarisation axis of the control laser. The mixing of the two lowest pendular states is provided *via* a

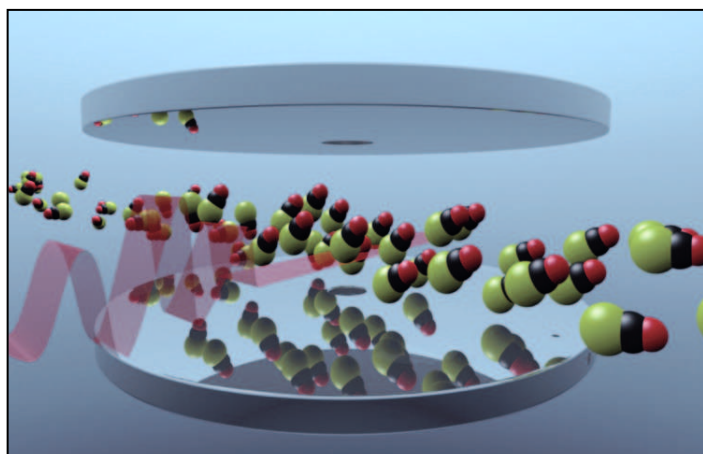


Figure 2

Artistic view of the collective orientation. A near-infrared laser (red) makes the originally disordered molecules perform synchronised cartwheels so that all the molecules at a particular position along the beam are oriented in the same direction.

non-adiabatic coupling by the fast rising and falling edges of the applied laser field. After the laser pulse, the resulting coherent superposition of the *s*- and *p*-rotor states propagates in time. This leads to an up-down-inverting oscillation of the dipole moment and the atoms of the molecule.

Figure 1 shows the experimental temporal evolution of the degree of orientation, in colour code, during and after the laser pulse. This is plotted, in the upper half of Fig. 1 for $\beta = 45^\circ$ and in the lower half of Fig. 1 for $\beta = -45^\circ$, as a function of the relative timing between the orientation and the probe laser pulses and of the peak intensity of the orientation pulse. After the former has been switched off a strong oscillatory behaviour was observed due to the coherent superposition of the field free *s* and *p* rotational states. A phase shift of π is observed when the polarisation of the laser field is rotated from $\beta = 45^\circ$ to $\beta = -45^\circ$ with respect to the static electric field.

Figure 2 shows an artistic view of the collective orientation. A near-infrared laser (red) makes the originally disordered molecules perform synchronised cartwheels so that all the

molecules at a particular position along the beam are oriented in the same direction — and this is repeated regularly, *virtually* forever.

The maximum orientation of the post pulse dynamics can be controlled, i.e., enhanced or suppressed, by the exact timing of the switching off and the intensity of the control pulse. This includes a complete population transfer into one of the involved states — effectively switching off all dynamics. To efficiently transfer the population back to the ground state, in our field configuration the falling edge of the laser pulse should start after a few nanoseconds, due to the slow dynamics of the field-dressed near-degenerate pendular states in the strong laser field. A complete transfer to the excited state, corresponding to a π -pulse, is obtained at exactly half of this time.

In summary, the preparation of molecules in a coherent superposition of free-rotor states of opposite parity results in strong, laser-field-free oriented samples. The mixing of the two states can be completely controlled by the combination of strong picosecond laser pulses and weak DC electric fields. Furthermore, simulations show that rapidly turning off the DC electric field, down to $\tau = 100$ ps, would not alter the wave packet dynamics and result in strong fully field-free orientation. The preparation of such ideal samples paves the way for novel experiments, such as electron and X-ray diffraction of small controlled molecules in the gas phase. In combination with molecular frame photoelectron angular distributions, complete molecular movies could be observed by simultaneous mapping of the molecular orbitals and the positions of the individual atoms during a chemical reaction.

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