

# Observing the rotation of molecules by following the evolution of the simplest wave packet

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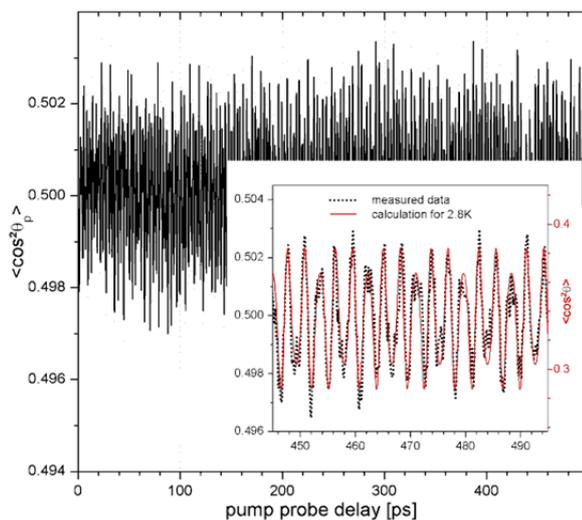
Coherent excitation of a superposition of discrete quantum states generates a quantum wave packet that evolves in time. In the specific case of rotational wave packets in molecules, this is observed as time-evolving alignment of the molecular axis or axes with respect to the laser polarization vector(s) [1, 2]. For most applications of the coherent alignment concept one desires rotationally-broad, spatially and temporally well-defined wave packets or, in other words, the highest possible degree of field-free alignment. It is important to note, however, that time-evolving rotational wave packets contain a wealth of information on molecular structures as well as insight into molecular coupling mechanisms such as rotation-vibration coupling, including both centrifugal and Coriolis interactions, and the interaction of molecules with their environment [3], which also changes their rotational constant  $B$ . Especially the investigation of molecules in quantum fluids is one of the 'hot' topics of contemporary chemical physics [4-6]. The fascination here derives from elucidating whether molecules can be used to reveal the properties of the surrounding quantum fluid as the number of atoms in the fluid changes. The use of alignment techniques for this purpose appears straight-forward. However, for such applications, one may need another approach, as in a typical experiment one has to disentangle the contributions of all cluster sizes in the molecular beam and very weak couplings leading to long decoherence times that are involved.

Rotationally broad wave packets as normally generated are not suitable for that purpose, as they undergo coherent dephasing due to the centrifugal distortion present at higher rotational quantum numbers. The other, much less frequently studied extreme is a superposition of just two rotational levels. This results in a very simple beat structure and can be understood as the most rudimentary form of a "wave packet" with an interesting property: it does not dephase and only perturbations cause decoherence. Hence, decoherence is not entangled with coherent dephasing.

In our recent beamtime we were able to demonstrate the feasibility of this approach. We followed the evolution of such a simple wave packet for more than 300 beating periods of the coherent superposition of  $J=0$  and  $J=2$  rotational states of CO after excitation using a near infrared Ti:sapphire laser system. The linearly polarized laser field induces non-resonant Raman transitions between rotational states. To keep the number of states to a minimum, short pulses (70 fs) were focused into a beam of CO molecules, resulting in a moderate intensity of less than  $5 \times 10^{12}$  W/cm<sup>2</sup> [7]. These conditions effectively limit the pumping process to a single Raman cycle. The target was prepared by expanding a gas mixture of 1% CO in helium at stagnation pressures between 5 and 50 bar into a vacuum chamber using a 100  $\mu$ m diameter, pulsed conical (20° half opening angle) nozzle of the Even-Lavie design. The pulsed valve generates a supersonic jet of sufficiently cold molecules. The jet passed through a skimmer and was directed between the extractor and repeller plates of a velocity map imaging (VMI) detector. The setup also served as a linear time-of-flight mass filter and allowed mass-selective detection to improve the signal-to-noise ratio. The alignment was probed as a function of time delay by Coulomb explosion of the molecules upon interaction with soft X-ray pulses from FLASH at a wavelength of 13.5 nm and with an average pulse energy of 30  $\mu$ J. The images of the two-dimensional momentum distributions

were acquired and stored on a single shot basis and the degree of alignment was extracted in real time during the measurements. We have put an emphasis to reduce the necessary shots per delay to a minimum to allow long and fast pump-probe-scans. In fact, we have seen that single shot measurements are feasible.

Figure 1 shows a pump-probe scan recorded at 14 bar stagnation pressure. The asymmetry parameter,  $\langle \cos^2 \theta_p \rangle$ , varies periodically with the pump-probe delay, as expected when exciting a coherent rotational wave packet. Contrary to the sharp full, half, and quarter revivals at the corresponding fractions of the revival time  $T_r=1/2B$  commonly observed in studies of rotationally-



**Figure 1:**

Anisotropy observed in a pump-probe scan ( $p_0=14$  bar) averaged over 25 shots per delay. The inset shows a comparison of the measured signal with a theoretical prediction for a rotational temperature of 2.8 K.

broad wave packets, the prevailing structure is a sine-like modulation with a period of  $1/3T_r$ , fundamentally different to wave packet revivals. As intended, a broad rotational wave packet is not created. Instead, we directly observe the phase evolution of the coherent superposition of the two quantum states coupled in the Raman cycle, or in other words the transition frequency  $f(J, J+2)=(4J+6)B$ , where  $J=0$  is dominantly populated in the beam. A closer inspection of the

pump-probe data reveals an additional weak modulation on top of the dominating structure. This originates from a subset of CO molecules in the  $J=1$  state, which are thermally populated in our sample. As illustrated in the inset of fig.1, the measured profiles at 14 bar agree perfectly with our calculations for a rotational temperature of 2.8 K of the molecular ensemble. In our supersonic beam experiments, rotational decoherence could be caused by collisions with other molecules or through absorption or emission of microwave photons. Neither process is relevant within the time window considered here. Hence, the signal modulations prevailed for more than 300 periods with no declining amplitude. The rotational constant deduced from the data is  $B=57631(25)$  MHz corresponding to  $1.9224(9)$   $\text{cm}^{-1}$  and matches microwave data within the error bars [8]. The demonstrated technique can now be used to track the evolution of the rotational constant with the number of attached helium atoms or more generally to observe intra- and intermolecular couplings leading to decoherence of rotational motion in complex systems and environments. It may be seen as performing microwave spectroscopy without microwaves at modern 4th generation free-electron laser sources such as FLASH creating new opportunities because the accessible energy range now extends from X-rays all the way down to microwaves. The combination of atomic resolution and fs precision with quantum state-selective techniques for preparing rotational wave packets promises unique insight into molecular structure and dynamics.

## References

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