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Generation of the simplest rotational wave packet in a diatomic molecule: Tracing a two-level superposition in the time domain

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We introduce a new time-domain approach to explore rotational dynamics caused by intramolecular coupling or the interaction with dissipative media. It pushes the time resolution toward the ultimate limit determined by the rotational period. Femtosecond pulses create a coherent superposition of two rotational states of carbon monoxide. The wave packet motion is observed by subsequent Coulomb explosion, which results in a time-dependent asymmetry of spatial fragmentation patterns. The asymmetry oscillation prevails for at least 1 ns covering more than 300 periods with no decoherence. Long time scans will allow weak perturbations of the order of $\Delta E/E = 10^{-4}$ to be discerned. Our conclusions are confirmed by a fully quantum-mechanical model.

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Coherent excitation of a superposition of discrete quantum states generates a quantum wave packet that evolves in time. Characteristic wave packet revivals are observed after the excitation pulse if the induced perturbation is short (impulsive) compared to the system response [1]. In the specific case of rotational wave packets in molecules, the revivals express themselves as time-evolving alignment of the molecular axis or axes with respect to the laser polarization vector(s) [2, 3]. This concept was pioneered by Zewail and coworkers in the late 80's and leads to well-known revival structures under field-free conditions [4]. The impact of this approach to alignment in many areas of ultrafast science and gas phase spectroscopy is extensive, ranging from molecular orbital tomography [5], single molecule imaging [6], laser pulse compression [7], high-order harmonic [8] and attosecond pulse generation [9] to fundamental studies on rotational coherence decay [10], and may even open new vistas for quantum computing [11] or the analysis and control of stereochemical reactivity [12].

For most applications of the coherent alignment concept one desires rotationally-broad, spatially and temporally well-defined wave packets or [13], 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 [14] as well as insight into molecular coupling mechanisms such as rotation-vibration coupling, including both centrifugal and Coriolis interactions [15], and the interaction of molecules with their environment

[16]. This information is available also from the time evolution of coherent wave packets containing contributions from only a few energy levels. We note, moreover, that the rate of coherent dephasing scales as the square of its width in the quantum number space. Rotationally broad wave packets undergo relatively fast dephasing due to the quadratic nature of rotational spectra. The other, much less frequently studied extreme is a superposition of just two rotational levels by means of fs pulses. 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. A two-level rotational superposition is therefore well suited to study intra- and intermolecular couplings leading to ultrafast decoherence of rotational motion in complex systems and environments. While the principle of this approach is equivalent to microwave spectroscopy in the time domain, it has the advantage of accessing the sub-ps time domain, where a variety of ultra fast phenomena of interest such as chemical reactions take place. Powerful techniques such as Fourier-Transform microwave spectroscopy (FTMW) have been much improved in recent years, providing excellent sensitivity and selectivity (the energy resolution has been pushed below 10^{-8} cm^{-1} corresponding to 1 kHz frequency resolution). However, even with the newly developed broadband microwave spectroscopy technique, the fastest response currently detected is in the region of 100 ps [17]. Furthermore, traditional FTMW requires molecules with

a permanent electric dipole moment – a restriction that does not apply to time-domain spectroscopy using impulsive excitation with fs laser pulses. Here, a two-photon Raman transition is induced by the interaction of the electromagnetic wave with the anisotropy of the molecular polarizability, making it complementary to microwave spectroscopy.

In this letter we report on the impulsive excitation of a rotational wave packet that consists of only two quantum states of carbon monoxide (CO) molecules. It was possible to follow the coherent nuclear motion with ≈ 100 fs resolution for a time period as long as 1 ns. The measurement covers more than 300 periods, making it possible to extract the contributing transition frequencies with a precision of a few hundred MHz. Although the alignment of state-selected molecules has recently been demonstrated experimentally [18], the preparation of molecules in specific quantum states remains a challenge [19, 20]. With few exceptions, e.g. hydrogen [21, 22], the rotational motion of a two-state superposition in the ultrafast limit has not been observed so far [23].

In the present experiment the coherent superposition of $J = 0$ and $J = 2$ rotational states of CO is excited using a 10 Hz Ti:sapphire laser system with 800 nm center wavelength. The linearly polarized laser field induces non-resonant Raman transitions according to the selection rules $\Delta J = 0, \pm 2$. The number of coupled rotational states in subsequent Raman cycles depends on the intensity and pulse duration of the pump pulse. To keep the number of states to a minimum, short pulses (70 fs) were focused into a beam of cold CO molecules, resulting in a moderate intensity of less than $5 \cdot 10^{12}$ W/cm² [24]. 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 different stagnation pressures between 5 and 50 bar into a vacuum chamber using a 100 μ m diameter, pulsed conical (20° half opening angle) nozzle of the Even-Lavie design. Under these conditions the pulsed valve generates a supersonic jet of sufficiently cold molecules, i.e. less than 3 K. The jet passed through a skimmer with 1 mm diameter and was directed between the extractor and repeller plates of a velocity map imaging (VMI) detector. The characteristic field-free revivals were probed as a function of time delay by Coulomb explosion of the molecules upon interaction with soft X-ray pulses from a free-electron laser (FEL) [25]. The FLASH facility at DESY in Hamburg provided intense FEL pulses with an average pulse energy of ≈ 30 μ J throughout the present studies. The machine was tuned to a photon energy of 92 eV and operated with a repetition rate of 10 Hz. The pulse duration of ≈ 50 fs gives an intensity of 10^{13} W/cm², sufficient to multiply ionize small molecules at the intersection point. The FLASH laser beam was guided collinearly with the pump laser beam in vacuum, intersected the supersonic jet and was dumped afterwards. The polarization of both

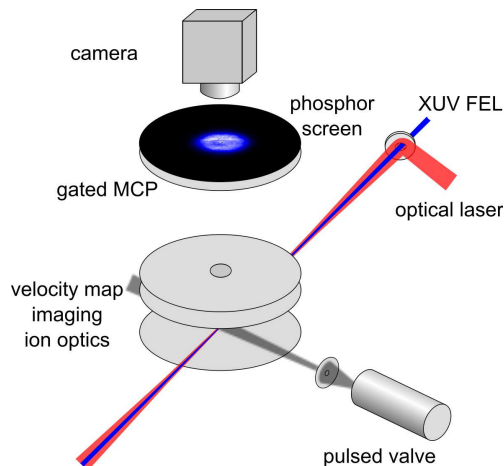


FIG. 1. (Color online) – Scheme of the experimental setup. The collinear near-infrared and XUV beams are both focused into the center of the ionization region of a velocity imaging spectrometer. They intersect there with the molecular beam entering the spectrometer through a 1 mm skimmer. The delay between the two laser pulses can be varied by a delay line in the infrared laser path (not shown). The ions created by the XUV pulse are projected to a MCP, where a mass gate can be selected by switching the applied voltage. The resulting images taken with a CCD camera are stored with 10 Hz.

laser pulses was parallel to the detection plane. We note that the peak intensity of the near-infrared laser was kept well below the threshold for ionization. The experimental layout is depicted in Fig. 1. Our experiments were complemented by quantum mechanical calculations of the rotational wave packet dynamics. These calculations served the dual purpose: (i) to compare experimental observables with molecular alignment characteristics and (ii) to determine the rotational temperature. The theory is elaborated in ref. [2]. In brief, the time-dependent wave packet is expanded in terms of spherical harmonics, eigenstates of the field-free rotational Hamiltonian, converting the time-dependent Schrödinger equation into a set of coupled differential equations for the expansion coefficients. The latter are propagated numerically to generate the wave packet (and hence all observables) as a function of time. Finite temperature is taken into account by Boltzmann averaging the observables.

The velocities of the ion fragments produced in the Coulomb explosion were measured using a home-built VMI detector [26]. It projects the three dimensional velocity distribution onto the position sensitive detector consisting of a micro channel plate (MCP) assembly, a phosphor screen and a CCD camera. The setup also served as a linear time-of-flight mass filter and allowed mass-selective detection to improve the signal-to-noise ratio. This was achieved by gating the voltage on the MCP stack at distinct time-intervals after the FEL light pulses. To maximize sensitivity to CO, the MCP was gated to the C^+ mass. Although images corresponding to

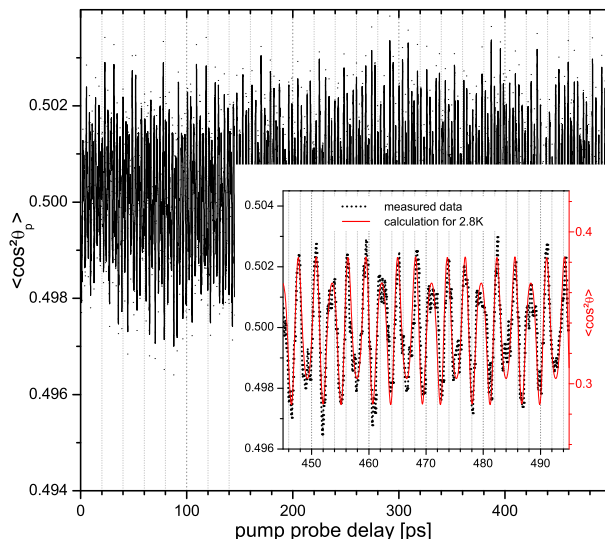


FIG. 2. (Color online) – Anisotropy observed in a pump-probe scan ($P_0 = 14$ bar) averaged over 25 shots per delay. The inset shows a comparison of the measured signal with a theoretical prediction for a rotational temperature of 2.8 K.

the O^+ mass revealed results indistinguishable from those corresponding to the C^+ mass, the latter was preferred to avoid a possible contribution from water in the residual gas. We note that the recorded momentum distributions are isotropic without the near-infrared alignment pulse indicating that the CO ionization cross section is almost isotropic for non-resonant XUV radiation. The images of two-dimensional momentum distributions of mass- and charge-selected ionic fragments were collected and stored for each FEL light pulse.

The degree of alignment of a diatomic molecule is generally quantified by means of the anisotropy or alignment parameter, $\langle \cos^2 \theta \rangle$, where θ is the angle between the molecular axis and the laser polarization. The value of $\langle \cos^2 \theta \rangle$ ranges between 0 (anti aligned) and 1 (perfectly aligned to the laser polarization), with $1/3$ being the value for an isotropic sample of molecules. Measuring this anisotropy parameter requires an inverse Abel transformation to deduce the full three-dimensional momentum distribution of the ionic fragments. Here, we used a slightly modified alignment parameter, $\langle \cos^2 \theta_p \rangle$, which was deduced directly from projected 2D momentum distribution images by using the angle θ_p between the molecular axis and the polarization in the projection on the two-dimensional detector plane. The value of this modified parameter for an isotropic sample is $1/2$ rather than $1/3$. While carrying the same information, this approach allowed us to omit the Abel transformation. As the Abel transformation introduces some additional noise, a clearer image with a higher number of detected ions would be needed to properly calculate the 3D momentum distribution. Omitting the transformation and integrating over all ion kinetic energies give two advan-

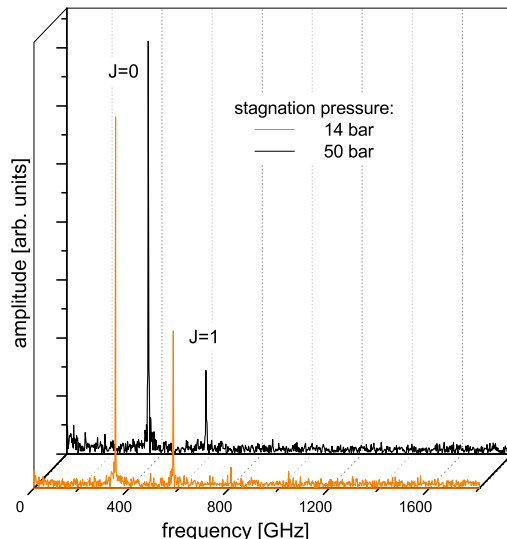


FIG. 3. (Color online) – Fourier transforms of two pump-probe scans under different expansion conditions. The frequency domain data clearly shows that the signal is dominated by the $J(0 \rightarrow 2)$ transition, with increased $J(1 \rightarrow 3)$ contribution at higher temperature or lower pressure, respectively.

tages: an improved signal-to-noise ratio of the modified alignment parameter and a vastly reduced computational effort. This makes it possible to reduce the time required for a pump-probe scan, since fewer ions need to be detected for each delay. In fact we have seen that single-shot measurements are feasible. We derived the modified alignment parameter in real-time during the measurement for each individual shot, which proved very useful when dealing with small degrees of alignment barely noticeable from the images themselves.

Figure 2 shows a pump-probe scan recorded at 14 bar stagnation pressure. The modified asymmetry parameter, $\langle \cos^2 \theta_p \rangle$, varies periodically with the pump-probe delay, as expected when exciting a coherent rotational wave packet. But contrary to the sharp full, half, and quarter revivals at the corresponding fractions of the revival time $T_r = \frac{1}{2B}$ commonly observed in studies of rotationally-broad wave packets, a different pattern appears under our chosen conditions. The prevailing structure is a sine-like modulation with a period of $\frac{1}{3}T_r$, fundamentally different to wave packet revivals. The reason is that the dominant excitation is the transition between the $J = 0$ and $J = 2$ rotational states: a broad rotational wave packet that dephases and revives is not created here. 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 $f(J \rightarrow J+2) = (4J+6)B$. 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. 2, the measured profiles at 14 bar agree perfectly with our calculations for a rotational temperature of 2.8 K of the molecular ensemble. The Fourier transform of the delay scans, as depicted in fig. 3, provides a map of the occupied rotational states. 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 1 ns time window considered here and 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 $1.9224(9)$ cm⁻¹ and matches microwave data within the error bars [27].

Several important conclusions can be drawn from the real-time observation of the simplest rotational wave packet composed of two quantum states. The quest for ultrafast microwave spectroscopy is key to understanding complex intra- and intermolecular couplings in large molecular systems. The recent development of chirped-pulse FTMW promises to overcome the traditional limitations in spectral bandwidth and data acquisition speed [28]. For instance, the isomerization reaction rates of vibrationally excited cyclopropane carboxaldehyde (c-C₃H₅CHO) initiated by internal rotation about a C-C bond have been measured with a time resolution of the order of 100 ps limited by the sampling rate [17]. We emphasize that with our method the time resolution to elucidate fast dynamics, i.e. strong couplings, can be pushed in general toward a single rotational period even for the fastest rotors. At the other limit of the time scale, the long intrinsic decoherence time makes large pump-probe delays with small sub-ps step size possible. This improves the accuracy of the derived rotational constants and introduces a new possibility to measure weak molecular couplings, as well as to explore in detail the population relaxation and phase decoherence of molecules in solutions or molecules dissolved in quantum fluids. Thus, a detailed analysis of small perturbations of the order of $\Delta E/E = 10^{-4}$ is feasible. An example of where this would be particularly valuable is the case of doped helium nanodroplets [29]. Helium droplets show exceptionally weak interaction with the rotation of molecular dopants in the superfluid phase. Current theoretical models predict that the non-superfluid density in helium droplets is increased near molecular impurities and is generally dependent on the rotational state [30]. Two-level rotational wave packets introduce an ideal tool to investigate the structure and dynamics of superfluid and non-superfluid helium in response to rotational excitation of a dopant. In principle, conventional broad (many state) rotational wave packets allow for these measurements too, providing even richer information since they also show the decoherence of different J levels. However, many different cluster sizes are present in the molecular beam. The sim-

ple two-level beat pattern allows for straightforward assignment of individual rotational constants whereas the evaluation in the case of a broad rotational wave packet becomes increasingly complex. Importantly, the method is not restricted to molecular systems that exhibit permanent electric dipole moments. In fact non-resonant, two-photon Raman excitation only requires anisotropy of the molecular polarizability, which in turn allows the study of coupling phenomena in homonuclear molecules and in clusters with zero or very small dipole moments. Last but not least, performing microwave spectroscopy without microwaves at modern 4th generation free-electron laser sources such as FLASH creates 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.

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