Experimental Observation of Revival Structures in Picosecond Laser-Induced Alignment of I_2

F. Rosca-Pruna and M. J. J. Vrakking*

FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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We report the experimental observation of revival structures in the alignment of a ground-state rotational wave packet following nonresonant excitation of I_2 molecules by an intense picosecond laser pulse. The revivals appear at characteristic time delays following the excitation by the pump laser pulse, and show a significant narrowing of the angular distribution during a few picoseconds. The interaction with the pump laser also leads to a steady-state alignment of the molecule, due to rotational pumping.

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There has recently been increasing awareness that intense femtosecond lasers can be used to control the properties of matter on a microscopic level. A new field of "molecular optics" is emerging, where intense lasers are used to manipulate the internal and the external degrees of freedom of molecules [1]. Lasers have been used to deflect beams of molecules [2], to control molecular dynamics [3], and to dissociate molecules in an "optical centrifuge" [4]. Considerable attention has been devoted to the ability of intense laser fields to align molecules (dynamic alignment), where molecules experience a torque due to the polarization induced by the laser. The role of dynamic alignment in multielectron dissociative ionization (MEDI) has been considered [5] and the formation of pendular states in the presence of a strong laser field has been firmly established [6–8]. Recently, Stapelfeldt *et al.* demonstrated the possibility of aligning molecules in three dimensions [9]. There have been a number of theoretical contributions on the possibility of aligning molecules both in a laser field [10] and under field-free conditions, *after* the excitation of a molecule by a short laser pulse. Seideman [11] and Friedrich and co-workers [12] performed calculations illustrating that the interaction of a molecule with an intense laser pulse can lead to the formation of a ground-state rotational wave packet (through Raman excitation), whose subsequent time evolution involves the formation of aligned molecular states at well-defined time delays with respect to the pump laser pulse, given by the rotational structure of the molecule.

In this paper we report what is, to our knowledge, the first experimental observation of revival structures in laser-induced alignment. Building on results which we have recently obtained for MEDI of I_2 [13,14], we present experiments where a picosecond pump laser is used to form a rotational wave packet in the ground electronic state of I_2, and where the angular distribution of the molecules with respect to the polarization axis of the pump laser is monitored as a function of time using a femtosecond probe laser pulse, which induces a Coulomb explosion of the molecules. The recoil velocity of the charged fragments in the Coulomb explosion is determined using a velocity map ion imaging detector [15,16]. We observe revival structures in the angular distributions which are reminiscent of revival structures observed in a number of rotational coherence spectroscopy experiments [17,18]. However, whereas in these other experiments the signal consists of time-dependent photon emission/scattering and/or molecular ionization, the measured signal in the present experiment is the time-dependent angular distribution of the molecules. Moreover, previous rotational coherence experiments were performed under conditions where the interaction with the laser(s) can be described by perturbation theory, whereas the present experiment relies on a strongly nonperturbative laser-molecule interaction. As a result, unlike the aforementioned experiments (where the rotational coherence signal is derived from a small subset of molecules in the sample), our experiment leads to the formation of a *macroscopic* sample of ground-state aligned molecules. This has important implications for the utility of the current technique. Aligned molecules prepared in this fashion can be used in a range of applications, such as studies of photoelectron angular distributions, where the measurements are no longer limited to a determination of a β parameter (averaging over all possible molecular alignments in the laboratory frame), but where the angular distributions can be studied directly in the molecular frame [19].

In the experiment, the output from a home-built 50 Hz Ti:sapphire femtoscond laser amplifier, delivering uncompressed pulses near 800 nm with a pulse energy up to 80 mJ, was split and compressed in two dual grating compressors. One beam, containing 30% of the energy, was compressed to a 100 fs pulse, and was used to probe the alignment via MEDI. After attenuation, this beam was typically used at a 1.2 mJ pulse energy. The second beam, containing 70% of the pulse energy, was compressed to pulse durations of 1–10 ps, and was used to align the molecules. After variable attenuation and delay of the pump laser beam, both beams were recombined on a beam splitter ($R = 30\%$, $T = 70\%$ for p polarization, $R = 50\%$, $T = 50\%$ for s polarization) and focused collinearly into the molecular beam apparatus, using a 20 cm lens. A telescope reduced the spot size of the pump laser beam on the

lens, to ensure that the probe laser focus was smaller than the pump laser focus. A molecular beam was formed by passing Ne gas over an I_2 sample and expanding the mixture through a 1 mm pulsed nozzle, located 5 cm in front of a 1.5 mm skimmer separating the source and the experimental chambers. The laser beams intersect the molecular beam at the center of a velocity map imaging detector [15,16]. The axis of the lasers, molecular beam and the imaging detector were orthogonal to each other [13]. The charged fragments were projected onto a dual microchannel plate (MCP) followed by a phosphor screen. The MCP-phosphor assembly was gated to enable detection of individual charge states. A CCD camera was used to record the 2D distributions on the phosphor screen. Recorded images were transferred to a laboratory computer, where a peak-finding routine determined the centroids of the observed spots on the phosphor screen, and where the images were accumulated. The pump laser polarization was along the molecular beam axis (in the plane of the MCP detector), and the probe laser polarization was along the detector axis (perpendicular to the MCP detector). As a result of this choice, the signal from the probe laser alone had no angular dependence on the detector, whereas changes in the angular distribution as a result of the interaction with the pump laser could readily be observed. Detection of both I^+ and I^{2+} was used.

In Fig. 1, a number of representative I^{2+} images are shown for four delays between the probe laser and a 3.8 mJ, 2.8 ps pump laser. In Fig. 1(a), an image is shown where the probe laser precedes the pump laser by 17 ps. Two rings are observed which, on the basis of their recoil velocity, correspond to the formation of I^{2+} with I and I^+. There is no angular dependence in either channel since the ionization does not depend on the azimuthal angle around the probe polarization axis. In Fig. 1(b), an image is shown where the probe laser is overlapped in time with the pump laser. Because of dynamic alignment, the I^{2+} angular distributions, which now also contain a small contribution of $I^{2+} + I^{2+}$, are nonisotropic and peaked along the pump laser polarization axis. Figures 1(c) and 1(d) show images recorded at long pump-probe time delays of 212 and 220 ps, respectively. At these delays, rapid changes in the angular distribution occur.

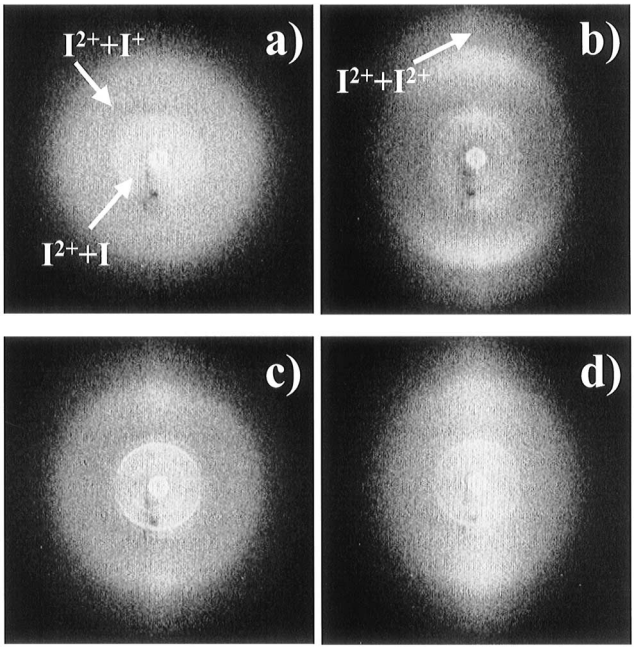

FIG. 1. Raw I^{2+} images, recorded with a 3.8 mJ 2.8 ps pump laser (polarized parallel to the plane of the imaging detector along the vertical axis of the image) and a 100 fs 1.2 mJ probe laser (polarized perpendicular to the imaging detector). (a) With the probe preceding the pump by 17 ps; (b) with the pump and probe lasers overlapped in time ($\Delta t = 0$ in Fig. 2); (c) with the pump preceding the probe by 212 ps; (d) with the pump preceding the probe by 220 ps.

A series of measurements was performed where images were recorded as a function of the time delay between the pump and probe lasers. Results of these measurements are shown in Fig. 2, where the labels (a)–(d) refer to the measurements shown in Fig. 1. In this figure, the time evolution of the angular distribution is shown by plotting the effective angular width α of an ionization channel, defined by the equation

$$\int_{\varphi=0}^{\varphi=\alpha/2}\int_{R=R_{\min}}^{R=R_{\max}} \mathrm{I}(R,\varphi)\,d\varphi\,dR \Big/ \int_{\varphi=0}^{\varphi=\pi/2}\int_{R=R_{\min}}^{R=R_{\max}} \mathrm{I}(R,\varphi)\,d\varphi\,dR = \frac{1}{2},$$

where φ is the angle with respect to the vertical axis of the image ($0 \le \varphi \le \pi/2$), and where $R_{\min}$ and $R_{\max}$ define the minimum and the maximum radius in the image where the contribution from a particular charge combination $I^{n+} + I^{m+}$ appears. This definition was chosen because it provides a simple one-parameter characterization of the angular width which is applicable for arbitrary (i.e., aligned and nonaligned) angular distributions. If the angular distribution is Gaussian, then α is equal to 0.69 times the full width at half maximum of this Gaussian. For an isotropic angular distribution α is 90°. In Fig. 2, no alignment appears when the probe laser precedes the pump laser ($\Delta t < 0$). The fact that α slightly deviates from 90° is due to a small segment on the imaging detector where the detection efficiency has degraded due to extensive use of the detector and a weak pump-only background signal. When the pump and probe lasers overlap in time, the onset of the alignment is observed. In the $I^{2+} + I^{2+}$ channel, α decreases by as much as 50°. At the end of the pump laser pulse, the alignment decreases. The angular width remains below the unpumped value however, since the pump laser interaction has shifted the rotational population to higher J. The experiment simultaneously measures the alignment starting from all rotational levels $(J_{\text{initial}}, M_{\text{initial}})$ which are initially populated in the sample. Since $\Delta M = 0$ for

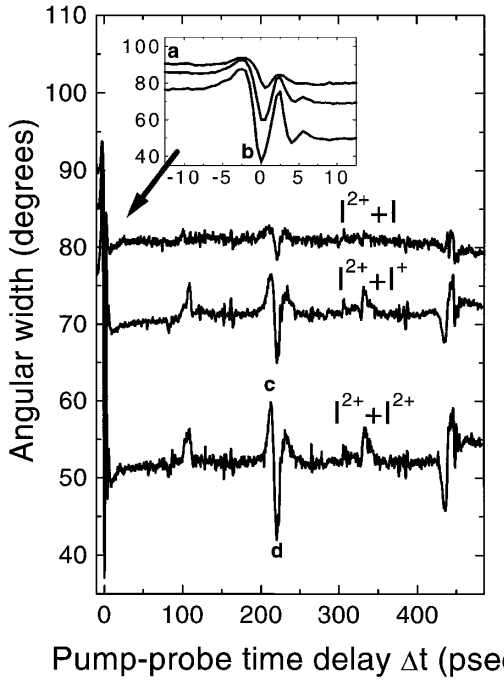

FIG. 2. Pump-probe time delay scan, showing the angular width α of the $I^{2+} + I$, the $I^{2+} + I^{+}$, and the $I^{2+} + I^{2+}$ channels, recorded using a 3.8 mJ 2.8 ps pump pulse and a 1.2 mJ 100 fs probe pulse. The measurements show alignment of the molecule during the pump pulse (see inset), residual alignment at the end of the pump pulse, and the occurrence of rotational revivals. The labels (a)–(d) refer to the measurements shown in Fig. 1.

excitation with linearly polarized light, the M distribution is conserved in this excitation process. Therefore a shift in the rotational distribution to higher J leads to a nonstatistical population of levels with $J > M_{\text{initial}}$, which shows up as a moderate alignment.

At well-defined time delays with respect to the time overlap of the pump and probe lasers, revivals are observed where α suddenly decreases or increases during several picoseconds. The observation of these revivals indicates that the pump laser has formed a rotational wave packet that keeps evolving after the pump laser interaction has ceased. From the rotational level structure, it follows that a full revival of the wave packet is expected at a revival time $T = 1/2Bc$, which is 450 ps for the I_2 molecule ($B = 0.037\ \text{cm}^{-1}$). A strong revival is observed around this delay. In addition, significant partial revivals are observed at delay times $T/4$, $T/2$, and $3T/4$. At revival times, a rephasing of the wave packet occurs so the molecule is once more strongly aligned along or perpendicular to the polarization axis of the pump laser.

A remarkable feature of the measurements shown in Fig. 2 is the fact that the alignment manifests itself more strongly in the highest charge channel $I^{2+} + I^{2+}$. This is surprising, since molecules aligned along the pump laser polarization axis are aligned orthogonally to the probe laser polarization axis, and are therefore difficult to ionize. Accordingly, we clearly observe that the intensity of the probe laser signal anticorrelates with the appearance of alignment. The fact that the highest charge states show the highest degree of alignment is probably due to a volume effect: At the common focus of the pump and probe lasers, the alignment forces are strongest, and the probe laser intensity is highest, enabling the formation of higher charge states.

We have investigated the occurrence of alignment during the pump laser pulse, the residual alignment after the interaction with the pump pulse, and the occurrence of revivals in the angular distribution as a function of a number of experimental parameters, such as the pump laser pulse duration and energy, the probe laser polarization, the expansion conditions of the molecular beam, and the charge state detected. The details of these experiments are the subject of a future publication [20]. In summary, we have observed how the alignment during the pump pulse is maximum for pump pulse durations of 3–5 ps, whereas the strength of the revivals is larger for pulse durations of 1–3 ps. The alignment during the pump pulse and on the revivals increases with laser pulse energy, though eventually it is limited by the initial rotational population in the sample. An example is shown in Fig. 3, where we

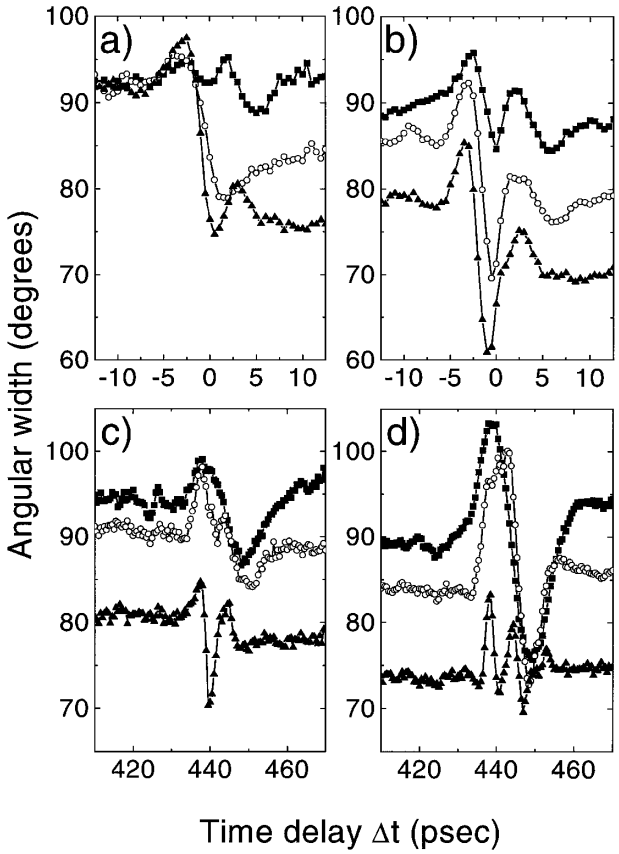

FIG. 3. Intensity dependence of the alignment with 1.4 ps pump laser pulses around the time overlap of the pump and probe lasers and at the full revival. (a) $I^{2+} + I$ around $\Delta t = 0$; (b) $I^{2+} + I^{+}$ around $\Delta t = 0$; (c) $I^{2+} + I$ around the full revival; (d) $I^{2+} + I^{+}$ around the full revival. The pump pulse energies used were 1 mJ/pulse (squares), 2 mJ/pulse (circles), and 3.5 mJ/pulse (triangles).

compare α near the time overlap of the pump and probe beams [Figs. 3(a) and 3(b)] and around the full revival time [Figs. 3(c) and 3(d)] for three pump laser pulse energies, in experiments carried out with a 1.4 ps pump laser pulse. Initially, the alignment increases with increasing pump energy, but then the decrease in the angular width saturates and rapid oscillations in α are observed.

We have performed model calculations on the interaction of an intense laser pulse with a diatomic molecule, which reproduce all qualitative aspects of the experiments presented here, and which suggest that in the current experiment the initial rotational temperature of the I_2 molecules (estimated to be 5–10 K based on resonance-enhanced multiphoton ionization measurements on N_2 carried out under similar conditions) eventually limits the minimum width in the angular distribution observed [20]. Narrower angular distributions are likely to be possible for lighter molecules, where the number of initial rotational states is more limited.

In conclusion, we have presented experiments on picosecond laser induced alignment of I_2 molecules, which demonstrate that it is possible to prepare a wave packet of ground-state rotational levels, which leads to a moderate steady-state alignment after the pump laser interaction, as well as the formation of an aligned sample of molecules at well-defined revival times. The molecules are aligned under field-free conditions, which distinguishes this form of alignment from the adiabatic alignment of molecules using long laser pulses, used by several other groups [7,8]. In the near future, we will attempt to use these aligned molecules to study molecular frame photoelectron angular distributions.

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*Email address: vrakking@amolf.nl

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