Impulsive Laser Induced Alignment of Molecules Dissolved in Helium Nanodroplets

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We show that a 450 fs nonresonant, moderately intense, linearly polarized laser pulse can induce field-free molecular axis alignment of methyliodide (CH_3I) molecules dissolved in a helium nanodroplet. Time-resolved measurements reveal rotational dynamics much slower than that of isolated molecules and absence of the sharp transient alignment recurrences characteristic of gas phase molecules. Our results presage a range of new opportunities for exploring both molecular dynamics in a dissipative environment and the properties of He nanodroplets.

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The ability to control how molecules are turned in space offers unique opportunities for studying and exploiting the ubiquitous orientational dependence of a molecule's interactions with other molecules, atoms, or polarized electromagnetic radiation and for eliminating the blurring of molecular properties and processes which usually occur in observations of randomly aligned molecules. For isolated molecules in the gas phase, intense laser pulses provide a versatile approach to sharply align molecules along axes fixed in the laboratory frame [1]. This ability has enabled a broad range of new applications in molecular science [2–5]. An intriguing question is whether laser induced alignment can be extended to molecules in dissipative environments. This has been studied for molecules in dense gases where collisions lead to relaxation of molecular alignment [6–11]. For molecules in a solvent no experiments and only a few theoretical works have been reported [6,7,12].

Laser induced alignment of isolated molecules is based on a nonresonant, intense laser pulse creating a coherent superposition of the quantum states that describe free rotation [1]. Transferring the approach to molecules in a solvent, however, faces several fundamental obstacles: (i) molecules in a classical solvent are not characterized by free rotation due to collisions with the solvent; (ii) even if a laser pulse could initiate coherent rotational motion, the collisions would destroy it so rapidly that no efficient alignment would be reached; (iii) the intense laser pulse would interact not only with the solute molecule but also with the solvent, for instance, through polarization or even ionization and, thereby, prevent efficient alignment. Laser induced alignment of molecules in a solvent may thus be sensitive to and, in the worst case, hindered by numerous mechanisms which are absent in vacuum.

The present experiment uses superfluid helium droplets [13–15] as a solvent because as a quantum fluid their unique properties strongly reduce the obstacles (i)–(iii). A liquid helium droplet is characterized by its ability to solvate almost any molecule and by its low polarizability and high ionization potential, which minimize its interaction with the laser light. The long rotational coherence times observed for embedded molecules through spectroscopy have been interpreted as free rotation of the molecules over several classical rotational periods within the 0.37 K ^{4}He superfluid [13–15], and they build the expectation that the He environment should be advantageous for laser induced alignment. Our work focuses on laser induced alignment in the nonadiabatic or impulsive regime where the laser pulse duration is much shorter than the classical rotational period T_{rot} of the molecule [16,17]. We show that when He droplets, singly doped with CH_3I molecules, are irradiated by a 0.45 ps long laser pulse, the molecules reach maximum alignment 17–37 ps later and, in another ~70 ps, return to random orientation which persists beyond 1000 ps. The dynamics differs completely from that observed for isolated CH_3I molecules where the first alignment maximum occurs 0.1–3.5 ps after the center of the pulse and recurs in regularly spaced (by ~33 ps), narrow time windows, termed revivals [1].

The principle of the experiment is illustrated in Fig. 1(a). The He droplets are formed by continuously expanding ~20 atm He gas, cryogenically precooled to 10–20 K, through a 5 μm orifice into vacuum. The average size of the droplets is determined by the temperature of the He gas and is $\sim 1.1 \times 10^4$ helium atoms per droplets at 12 K [13], the temperature used for most of our measurements. The droplet beam passes through a pickup cell, where the partial pressure of CH_3I is adjusted to optimize for single molecule doping of each droplet. Hereafter, the doped He droplet beam enters the target region where it is crossed, at 90°, by two collinear pulsed laser beams. The first pulse

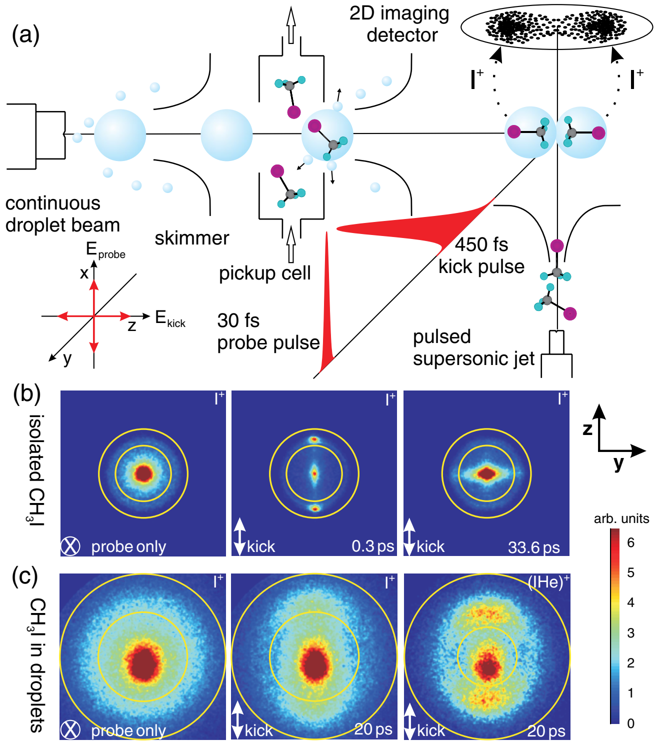

FIG. 1 (color online). (a) Schematic of the key elements in the experiment. The electrostatic plates projecting the I^+ ions onto the imaging detector are not shown. The polarization state of the kick and the probe laser pulses are shown in the coordinate system and indicated by the pulses. (b) I^+ ion images recorded for isolated CH_3I molecules with the probe pulse only, $t = 0.3$ ps and $t = 33.6$ ps with the polarization of the kick pulse indicated. (c) I^+ or IHe^+ ion images recorded for CH_3I molecules in He droplets with the probe pulse only and $t = 20$ ps. The dark red spot originates from ionization of background gas in the target region. It does not contribute to our determination of $\langle\cos^2\theta_{2D}\rangle$ which is based only on the ion signal in the area between the yellow circles. The velocity ranges depicted in all images in (b) and (c) are identical and the color scale for each image is normalized to the peak intensity outside the central dark red spot $I_{kick} = 1.2 \times 10^{13}$ W/cm^2.

(kick pulse, $\lambda = 800$ nm, $\tau_{FWHM} = 450$ fs) is used to induce alignment. The second pulse (probe pulse, 800 nm, 30 fs) is used to probe the molecular orientation. It is sufficiently intense ($I_{probe} = 1.8 \times 10^{14}$ W/cm^2) to multiple ionize CH_3I resulting in Coulomb explosion into positively charged fragments, notably I^+ with a CH_3^+ partner. These I^+ ions recoil along the molecular symmetry axis of the CH_3I parent molecule, and by detecting their emission direction with a velocity map ion imaging spectrometer, we determine the spatial orientation of CH_3I at the time defined by the delay t between the kick and the probe pulse [18]. A second molecular beam, containing isolated CH_3I molecules, can be sent into the target region (see Fig. 1). Thereby, alignment of isolated molecules and alignment of molecules in He droplets can be compared under identical laser pulse conditions.

Figure 1(b) shows examples of I^+ ion images from Coulomb explosion of isolated CH_3I molecules. When only the probe pulse is used, the I^+ image (left) is circularly symmetric as expected for randomly oriented molecules. When the kick pulse is included, the I^+ ions localize along (middle) or perpendicular (right) to the kick pulse polarization at certain times. At these times the C-I axis of the molecule is aligned or antialigned, respectively. The variation of the alignment angle θ_{2D} between the kick pulse polarization and the projection on the detector screen of the I^+ ion recoil velocity vector is quantified by the average, $\langle\cos^2\theta_{2D}\rangle$. It is determined only from those ions pertaining to the directional I^+-CH_3^+ Coulomb explosion channel marked by circles in Fig. 1(b).

The time dependence of $\langle\cos^2\theta_{2D}\rangle$ for isolated molecules is displayed in Fig. 2 (black curves) and can be explained by the formation of a rotational wave packet by the kick pulse [17]. When the kick pulse is applied $\langle\cos^2\theta_{2D}\rangle$ rises sharply to a local maximum at $t = 0.3$ ps. Hereafter, it drops quickly to a value of 0.64 and remains at this level except in narrow time windows, separated by $\sim$33.3 ps. These transients are the manifestations of full revivals ($t = 0.3$ ps $+ NT_{rot}, N = 1, 2, \ldots$) and half-revivals [$t = 0.3$ ps $+ (N - 1/2)T_{rot}$, $N = 1, 2, \ldots$], where $T_{rot} = 1/2Bc = 66.7$ ps for a rotational constant $B = 0.250\,\mathrm{cm}^{-1}$. The observations are fully consistent with many previous studies of impulsive alignment [16,19].

For the doped He droplet data the I^+ image recorded with the probe pulse only [Fig. 1(c), left] is also circularly symmetric. The radial (momentum) distribution is, however, much broader. We ascribe this mainly to the influence of the He atoms in the immediate surroundings of the molecule on how the I^+ and CH_3^+ ions share the kinetic energy released in the Coulomb explosion. After photodissociation of methyliodide, scattering on He atoms on the travel out of larger droplets explains a lowering of the kinetic energy of I atoms [20] that we do not observe for I^+ ions. To properly account for the broad momentum distribution, the radial range used

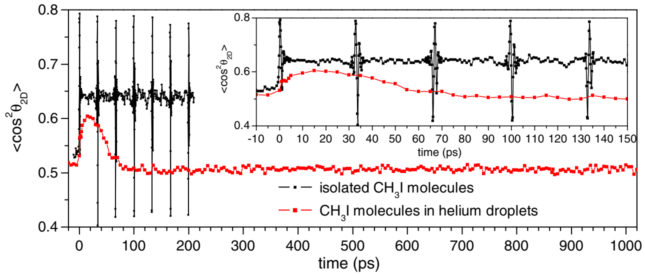

FIG. 2 (color online). The degree of alignment, represented by $\langle\cos^2\theta_{2D}\rangle$ determined from I^+ images, of isolated CH_3I molecules (black squares) and of CH_3I molecules in He droplets [gray (red) squares] as a function of time after the peak of the kick pulse (centered at $t = 0$). The parameters of the kick and the probe pulse are identical for the two data series. $I_{kick} = 1.2 \times 13$ W/cm^2. The inset expands on the first 150 ps.

to determine $\langle \cos^2\theta_{2D} \rangle$ has been adjusted; see Fig. 1(c). After the kick pulse, the I^+ ions localize along its polarization axis (middle panel), which is a clear manifestation of alignment. The same information is obtained from $(IHe_n)^+$ images, which only have a narrower radial distribution (right panel). The slight offset of the ion distributions from the center of the images (dark red spot) in Fig. 1(c) results from the velocity of the droplet beam (along the z axis) which, unlike the beam of isolated molecules, is parallel to the ion detector; see Fig. 1(a).

The time dependence of $\langle \cos^2\theta_{2D} \rangle$ for CH_3I molecules in He droplets is displayed by the gray (red) curves in Fig. 2. After ~20 ps $\langle \cos^2\theta_{2D} \rangle$ reaches a maximum of 0.60 demonstrating unambiguously that molecules can be aligned inside a He droplet under field-free conditions. The $\langle \cos^2\theta_{2D} \rangle$ curve differs strongly from the curve recorded for the isolated molecules. Not only is the rise time to the first alignment peak much longer (~ 20 ps versus 0.3 ps), it also decreases to a value of 0.5 with an isotropic image, which characterizes a sample of randomly oriented molecules, within ~100 ps. For the isolated molecules the prompt alignment decays within ~4 ps to a $\langle \cos^2\theta_{2D} \rangle$ value of 0.64, characterizing the time-independent permanent alignment [17], and regains high values at the revivals. For molecules in the droplets $\langle \cos^2\theta_{2D} \rangle$ stays constant at 0.5 for $t = 100$–1000 ps without any significant signs of revivals. Finally, the maximum degree of alignment observed, 0.60, falls below the maximum value of 0.78 obtained for the isolated molecules.

The lower values of $\langle \cos^2\theta_{2D} \rangle$ observed in the droplet case can partly be attributed to deviation from axial recoil in the Coulomb explosion process. Some of the He atoms in the immediate surroundings of the molecule are ionized and their electrostatic action on the departing I^+ ion may cause its recoil direction to deviate from the C-I axis of the parent molecule. Thus, the $\langle \cos^2\theta_{2D} \rangle$ values underestimate the true degree of alignment of the molecules inside the droplet as compared to the isolated molecules [21].

Our observations may at first seem at odds with expectations based on the prevailing conception of rotational structure and dynamics of molecules inside He droplets. Indeed, high resolution infrared and microwave absorption spectra have established that a gas phase Hamiltonian describes the rotational spectrum well with the effect of the He solvent being to reduce (increase) the rotational constants (moments of inertia) by up to a factor of ~5. This is commonly attributed to adiabatic following of a nonsuperfluid He solvation shell surrounding the solute molecule [15,22]. Thus, one might expect that the alignment dynamics would be similar to that observed for isolated molecules but slowed by up to a factor of ~5 due to the increased moments of inertia. By contrast, we observe that it takes the molecules ~10–170 times longer [23] to reach the first alignment maximum, i.e., a much slower rotational dynamics than expected.

To gain further insight into laser induced molecular alignment in He droplets the time dependence of $\langle \cos^2\theta_{2D} \rangle$ was recorded at different kick pulse intensities. In particular, the measurements were pushed towards as low intensities as possible, aiming at forming a wave packet composed of low lying rotational states, since these states have the longest lifetimes according to spectroscopic studies [15]. Thus, coherence between the rotational states should be allowed to survive sufficiently long that revivals could be formed. The reference measurements on isolated molecules [Fig. 3(a)] show that the revivals evolve from sharp to broad structures as the intensity is lowered, which is a clear manifestation that the wave packet changes from comprising a broad superposition of high lying states to just a few low lying states. In addition, the permanent alignment level, observed between the revivals, decreases due to excitation into gradually lower rotational states. The data for CH_3I in He droplets [Fig. 3(b)] show that the maximum degree of alignment gradually occurs at later times and gradually decreases as the intensity is lowered. There is, however, no sign of revivals at any of the intensities and the peak value stays slightly lower than the permanent alignment in the corresponding isolated molecule case.

To ensure that the alignment dynamics observed is not a result of some unusual behavior of CH_3I in He droplets, we repeated the measurements for carbondisulfide (CS_2) and iodobenzene (C_6H_5I) molecules. The time dependence of $\langle \cos^2\theta_{2D} \rangle$ for all three molecules is shown in Fig. 4. Although there are minor differences between the three curves, the overall alignment dynamics is very similar, whereas their alignment dynamics in the gas phase is

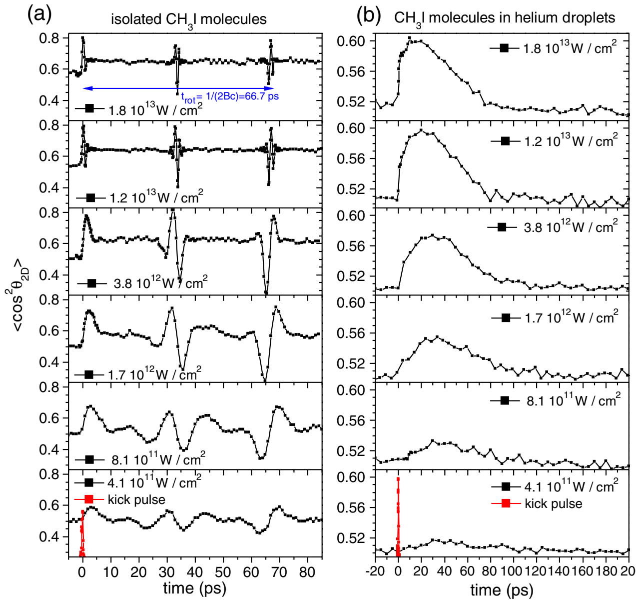

FIG. 3 (color online). $\langle \cos^2\theta_{2D} \rangle$ as a function of time, recorded at different intensities of the kick pulse and for both isolated CH_3I molecules (a) and CH_3I molecules in He droplets (b).

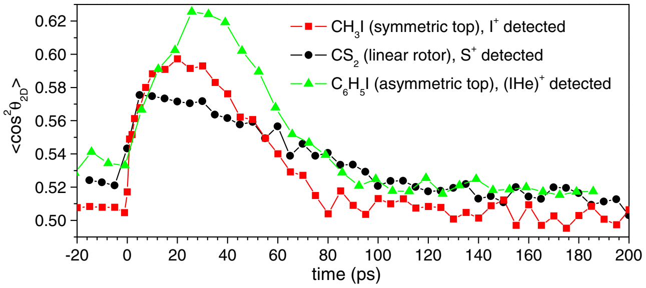

FIG. 4 (color online). $\langle \cos^2\theta_{2D}\rangle$ as a function of time, recorded for CH$_3$I (red squares), CS$_2$ (black circles), and C$_6$H$_5$I (green triangles) in He droplets. $I_{kick} = 1.2 \times 13\ \mathrm{W/cm^2}$.

significantly different [19,24,25]. Furthermore, we explored whether or not the alignment dynamics observed is sensitive to the size of the He droplet. In practice this was done by recording the time dependence of $\langle \cos^2\theta_{2D}\rangle$ for CH$_3$I in He droplets at temperatures of 12, 16, and 18 K of the expanding ~20 atm He gas. This corresponds to mean droplet sizes of ~11000, ~2000, and ~900 He atoms per droplet, respectively [13]. No significant differences between the three curves could be detected. The absence of any effect of the droplet size rules out several plausible explanations for the observed dynamics, such as an inhomogeneous effect due to the distribution of the droplet size, an influence of translational states of the embedded molecule within the droplet, a coupling to ripplons [14], or an overall rotation or deformation of the whole droplet.

The observed effects are not captured by the published theoretical works on the influence of a dissipative environment on nonadiabatic alignment of molecules [6,7,11]. In these works, correlations between the molecule and the surrounding particles are neglected, and the environment is taken into account by incorporating decoherence and population decay of the molecular rotational wave packet—induced by elastic and inelastic collisions—only *after* the pulse is switched off. The rotational wave packet coherence can indeed be lost due to collisions [8,9], but they would affect only the amplitude and not the period of the rotational motion [7,9,11,26]. This contradicts the observed dynamics which is much slower than the dynamics expected even for a moment of inertia 5 times larger than the gas phase value. Thus, the comparison of our results with the theoretical works indicates that interactions *during* the pulse and, possibly, correlations between the molecule and the helium droplet are influencing the dynamics.

This hypothesis is corroborated by comparing our experiment with microwave [22] and infrared spectroscopy [15] of molecules in helium droplets: At the lowest kick pulse intensities, only the lowest rotational states ($J \leq 4$), with long coherence lifetimes [15], are excited. The intensity of the kick pulse ($\sim 10^{11}\ \mathrm{W\,cm^{-2}}$) is, however, orders of magnitudes higher than the intensities ($\lesssim 10^2\ \mathrm{W\ cm^{-2}}$) used in spectroscopy. Rather than spectroscopically probing the rotational eigenstates of the coupled system, the kick pulse impulsively excites rotational motion of the molecule within the droplet, and the subsequent dynamics is not consistent with the long coherence times observed in spectroscopy. At the higher kick pulse intensities, we enter a regime of rotational states that is not investigated in He droplet spectroscopy and whose energies and lifetimes are not known. The absence of any discontinuity in the dependence on the kick pulse intensity [Fig. 3(b)] indicates, though, that similar mechanisms may explain the experiments at all intensities, and thus a complete understanding of the highly excited J states may not be needed to interpret our results.

The time dependence of the alignment at different kick pulse intensities and the only marginal dependence on the molecular species indicate that the droplet response to the molecular excitation is significantly influencing the observed dynamics. One potential effect is the exchange of angular momentum between the molecule and the helium environment—an effect starting already during, and possibly enhanced by, the kick pulse. The resulting scrambling of M values (M being the projection of the rotational angular momentum on the axis defined by the kick pulse polarization) implies that the rotational wave packet formed differs from the one created in isolated molecules (where $\Delta M = 0$ [19]) and may partly explain the slow rise. The M scrambling will continue after the kick pulse and together with the onset of population decay of rotational states it ultimately forces the alignment to decay towards the value of an isotropic ensemble—as observed. In addition, the impulsive excitation of the molecule may excite collective modes of the helium droplet which will be correlated with the different components of the rotational wave packet and, thereby, also influence the alignment dynamics. A full account of the details of the observed dynamics requires a quantitative many-body analysis of the coherent and dissipative molecule-solvent interactions, which is beyond the scope of this Letter.

To conclude, we have shown that a short, intense laser pulse can align molecules dissolved in He nanodroplets under field-free conditions. This opens many new opportunities, notably for time-resolved imaging of molecular frame reaction dynamics under influence from the dissipative environment of a solvent [27]. The ability of He droplets to dissolve molecules ranging from the smallest diatomics over biochromophores [28] to proteins [29] presage studies for a variety of species. The understanding of the slow rotational dynamics and the absence of revivals reported here calls for new theoretical descriptions, which could provide novel insight into the elementary excitations of He nanodroplets. In particular, rotational wave packets can transfer large amounts of angular momentum to the He surroundings and may be a way to explore quantized vortices [14,30–32], damping of collective modes, and their relation to the critical velocity in superfluid He droplets [33].

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