

Intense Laser Alignment in Dissipative Media as a Route to Solvent Dynamics

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We extend the concept of alignment by short intense pulses to dissipative environments within a density matrix formalism and illustrate the application of this method as a probe of the dissipative properties of dense media. In particular, we propose a means of disentangling rotational population relaxation from decoherence effects via strong laser alignment. We illustrate also the possibility of suppressing rotational relaxation to prolong the alignment lifetime through choice of the field parameters. Implications to several disciplines and a number of potential applications are proposed.

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Alignment by short intense laser pulses has been the topic of rapidly growing experimental and theoretical activity during the past few years, due to both the fascinating physics involved and the variety of already demonstrated and projected applications [1–13]. In the isolated molecule limit, corresponding to a molecular beam experiment, a moderately intense laser pulse of duration short with respect to the rotational time scales produces a broad wave packet of rotational levels through multiple angular momentum-nonconserving cycles, either between two or within one rotational manifold. The phase relationship between the rotational components, and hence the spatial properties of the wave packet and their time evolution, is determined by the temporal structure of the laser pulse and is thus largely controllable [6]. Depending on the pulse duration and intensity, the probability density aligns along the field polarization direction during or after the laser pulse and subsequently dephases [14], due to the anharmonicity of rotational spectra. Since coherence is maintained in the isolated molecule limit, the wave packet undergoes periodic revivals and fractional revivals, where the alignment is restored under field-free conditions. For linear and symmetric top molecules the initially created alignment is precisely reconstructed at multiples of the full rotational revival time [1].

Here we extend the concept of short-pulse-induced alignment to dissipative environments within a quantum mechanical, density matrix formalism. Our motivation is multifold. First, it may be expected (and is illustrated below) that the unique coherence properties of rotationally broad wave packets would provide a sensitive probe of the dissipative properties of the medium. In particular, we show that the experimental observables of alignment disentangle decoherence [14] from population relaxation effects (often referred to as T_1 and T_2 effects), providing independent measures of the relaxation and the decoherence dynamics that go beyond rate measurements. The potential of such measures is evident from several decades of intensive research on pressure broadening [15,16] and polarization spectroscopy [17,18], motivated by the realization that rotationally inelastic and elastic reorienting

collisions contain unique information about reaction mechanisms and pathways. To date, however, a general means of disentangling decay from decoherence or probing the dynamics of elastic collisions is lacking. Second, we expect laser alignment to become a versatile tool in chemistry, once the effects of dissipative media on alignment are properly understood. In particular, we anticipate applications of 3D alignment, as induced by elliptically polarized pulses, ranging from control of charge transfer reactions and new designs of molecular switches, through enhancement of NMR, EPR, and diffraction spectroscopies, to means of controlling molecular assembly in device fabrication. Likewise interesting, and the topic of ongoing study, is the application of rotational wave packets in the gas cell environment for quantum storage. Further impetus for extending the theory of alignment to dissipative media within a quantum mechanical framework comes from recent experiments on rotational coherence spectroscopy in a dense gas environment [19]. So far interpreted within a weak field approach, experimental work in this area has recently provided ample evidence for strong field effects [20], calling for a nonperturbative theory. Thus, both the case of alignment in a gas cell and that of alignment in solution are of formal interest and practical relevance.

In the present work we develop a general formulation within a quantum mechanical multilevel Bloch approach and focus on the dense gas case in numerical applications. We provide both model illustrations and realistic calculations for specific systems. The former serve to illustrate, in a completely general framework, the application of alignment as a probe of the dissipative properties of the medium. The latter serves to explore the extent to which field-free alignment may be expected to survive in dense environments and the degree to which the decay and decoherence rates can be controlled. For simplicity we limit attention to the common model of a rigid, linear molecule subject to a linearly polarized, nonresonant laser pulse. Our conclusions, however, are general.

A common measure of the degree and time evolution of the alignment is the expectation value of $\cos^2\theta$, where θ is the angle between the molecular axis and the field polar-

ization direction. In terms of the reduced density operator, $\hat{\rho}(t)$, this observable is given as $\langle \cos^2\theta \rangle = \text{Tr}\{\cos^2\theta \hat{\rho}(t)\}$. We note that $\langle \cos^2\theta \rangle$ is sensitive only to rotational coherences and rotational relaxation. The diagonality of the operator $\cos^2\theta$ with respect to all quantum numbers except for the angular momentum quantum number J follows from its dependence on a single coordinate, the polar Euler angle θ that is conjugate to J (in a rough sense). It thus disentangles the effects of J -changing collisions from those of purely M -changing collisions (M being the mag-

netic quantum number), and, in case a rovibronic wave packet is excited, also from the effects of vibrational and electronic relaxation and decoherence.

Accordingly, we expand the density operator in terms of rigid rotor eigenstates as $\hat{\rho}(t) = \sum_{J,M,J',M'} \rho_{JM,J'M'}(t) |JM\rangle \langle J'M'|$. The time evolution of the elements of the density matrix is given by the quantum Liouville equation, and in the context of a multilevel Bloch model for the dissipative operator [21], they obey the following equation of motion:

$$\begin{aligned} \frac{d\rho_{JM,J'M'}(t)}{dt} = & -\frac{i}{\hbar} \left\{ (\varepsilon_J - \varepsilon_{J'}) \rho_{JM,J'M'}(t) - \Omega_R(t) \sum_{J_1} [V_{JM,J_1M_1} \rho_{J_1M_1,J'M'}(t) \delta_{MM_1} - V_{J_1M_1,J'M'} \rho_{JM,J_1M_1}(t) \delta_{M'M_1}] \right\} \\ & - \left\{ \sum_{J_1M_1} \frac{1}{2} (K_{JM,J_1M_1} \rho_{JM,J'M'}(t) + K_{J'M',J_1M_1} \rho_{JM,J'M'}(t) - \delta_{JJ'} \delta_{MM'} 2K_{J_1M_1,JM} \rho_{J_1M_1,J_1M_1}(t)) \right. \\ & \left. + (1 - \delta_{JJ'} \delta_{MM'}) \gamma_{JM,J'M'}^{(pd)} \rho_{JM,J'M'}(t) \right\}, \end{aligned} \quad (1)$$

where $\Omega_R(t) = \frac{1}{4} \Delta \alpha \varepsilon^2(t)$, the polarizability anisotropy is defined in terms of the components of the molecular polarizability tensor as $\Delta \alpha = \alpha_{\parallel} - \alpha_{\perp}$, $\varepsilon(t)$ is the pulse envelope, $V_{JM,J'M'} = \langle JM | \cos^2\theta | J'M' \rangle$, and we note that optical transitions conserve M . The population transition rates between states $|JM\rangle$ and $|J_1M_1\rangle$ are given by K_{JM,J_1M_1} with $K_{JM,J_1M_1} = 0$. In Eq. (1), $\gamma_{JM,J'M'}^{(pd)}$ is the rate of pure dephasing of the $|JM\rangle \langle J'M'|$ coherence.

It is instructive to partition the alignment measure as

$$\langle \cos^2\theta \rangle \equiv \langle \cos^2\theta \rangle_{\text{tot}} = \langle \cos^2\theta \rangle_p + \langle \cos^2\theta \rangle_c, \quad (2)$$

where $\langle \cos^2\theta \rangle_p \equiv \sum_{J,M} \rho_{JM,JM}(t) V_{JM,JM}$ and $\langle \cos^2\theta \rangle_c \equiv \sum_{J \neq J', M} \rho_{JM,J'M}(t) V_{JM,J'M} = \sum_{J,J' = J \pm 2, M} \rho_{JM,J'M}(t) V_{JM,J'M}$. While formally the partitioning of a representation of $\hat{\rho}$ into diagonal and off-diagonal terms is always possible, in the context of alignment Eq. (2) carries interesting physical significance and important practical consequences. Its power owes to the fact that $\langle \cos^2\theta \rangle_p$ provides a direct experimental measure of the population elements, whereas $\langle \cos^2\theta \rangle_c$ measures directly the time evolution of the coherence elements of the density matrix. This property can be illustrated by expressing the $V_{JM,J'M}$ in terms of analytical functions, to provide explicit forms for the time evolution of $\langle \cos^2\theta \rangle_p$ and $\langle \cos^2\theta \rangle_c$. During the pulse each of the thermally populated levels $\{J_i, M_i\}$ is excited into a broad superposition of levels $\{J, M = M_i\}$; $\langle \cos^2\theta \rangle_p$ undergoes a sharp rise from $1/3$ to its maximum value ($\sim 1/2$ in the strong field, $\Omega_R \gg kT$ limit, where k is Boltzmann's constant and T is the temperature), and $\langle \cos^2\theta \rangle_c$ raises from zero to a maximum value that approaches $\frac{1}{4} \sum_{JM} (\rho_{JM,J+2M} + \rho_{JM,J-2M})$ in the strong field limit. In the isolated molecule case, $\langle \cos^2\theta \rangle_p$ is constant after the pulse turn-off, whereas $\langle \cos^2\theta \rangle_c$ oscillates with a constant amplitude at the rotational period. In a dissipative environment, $\langle \cos^2\theta \rangle_p = \frac{1}{3} \sum_{JM} \{1 + 2 \frac{J(J+1) - 3M^2}{(2J+3)(2J-1)}\} \rho_{JM,JM}$ describes a smooth baseline that decays from

$\max\{\langle \cos^2\theta \rangle_p(t)\} \sim \frac{1}{2}$ to its initial (thermal) value of $\frac{1}{3} \sum_J \sum_{M=-J}^J \{1 + 2 \frac{J(J+1) - 3M^2}{(2J+3)(2J-1)}\} \rho_{JM,JM} = \frac{1}{3}$, tracing accurately the decay of population due to inelastic (J -, or J - and M -changing) collisions. It follows that $\langle \cos^2\theta \rangle_p$ presents an experimental measure of the dynamics of population relaxation and is independent of decoherence, whereas $\langle \cos^2\theta \rangle_c$ responds solely to decohering processes. It is pertinent at this juncture to point out that the description of dissipation as given by Eq. (1) and the decomposition of the alignment observable $\langle \cos^2\theta \rangle$ in terms of $\langle \cos^2\theta \rangle_p$ and $\langle \cos^2\theta \rangle_c$ are general. In particular, they are equally valid for gaseous media and for solutions. System details are incorporated via the transition rates, $K_{JM,J'M'}$, whose form and magnitude depend on whether the interaction of the molecular system with its bath is via binary collisions, as in the case of a gaseous media, or in terms of a spectral function, as is typically the case with solutions.

In Figs. 1 and 2 we illustrate the application of alignment as a coherence spectroscopy of system-bath interactions. To that end we use model calculations that vary the elastic and inelastic transition rates in Eq. (1) in a range relevant to molecular systems and have the merits of simplicity and generality. We define system-independent, unitless time, intensity, and temperature variables as $\bar{t} = t/(\pi\hbar/B_e)$, $\bar{\Omega}_R = \Omega_R(t_0)/B_e$, and $\bar{T} = kT/B_e$, respectively, where B_e is the rotational constant and t_0 is the temporal center of the pulse. In Fig. 3 we examine the extent to which alignment is expected to survive in dissipative media and the controllability of the decay dynamics through choice of the field parameters. To that end we consider two specific systems for which the system parameters in Eq. (1) are available in the published literature (CO/Ar [16]; N₂/H₂O [15]), and which exhibit very different decay dynamics. For consistency with the population transfer rates available in literature [15,16], the $K_{JM,J'M'}$ terms are taken to be independent of M . The pure dephasing rate, $\gamma^{(pd)}$, was found negligible in several gas phase collisional systems

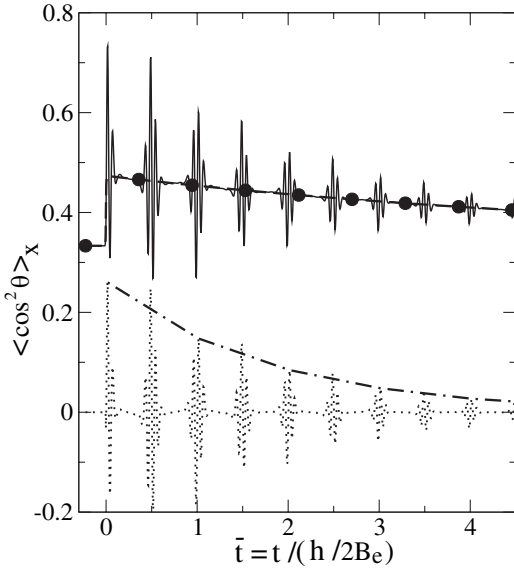


FIG. 1. The averaged alignment $\langle \cos^2 \theta \rangle$ (solid curve) and its components $\langle \cos^2 \theta \rangle_p$ (dashed curve and circles) and $\langle \cos^2 \theta \rangle_c$ (dotted curve) versus time, measured in units of the rotational period $\pi \hbar / B_e$. The interaction strength is $\bar{\Omega}_R = \Omega_R(t_0) / B_e = 291$, the pulse duration is $0.011 \pi \hbar / B_e$, and $\gamma^{(pd)} = 2.3 \pi \hbar / B_e$. The dot-dashed curve traces the amplitude of $\langle \cos^2 \theta \rangle_c$.

[17] and for N_2 systems was shown at most weakly J dependent [22]. In liquids, by contrast, pure dephasing plays a dominant role in the dissipation dynamics [23]. Here we include a weakly temperature-dependent $\gamma^{(pd)} \neq 0$ in the calculations leading to Figs. 1 and 2, as these serve as general model studies, and set $\gamma^{(pd)} = 0$ in Fig. 3, which pertains to realistic gas phase systems.

Figure 1 provides a pictorial illustration of the discussion surrounding Eq. (2), showing $\langle \cos^2 \theta \rangle$ (solid curve)

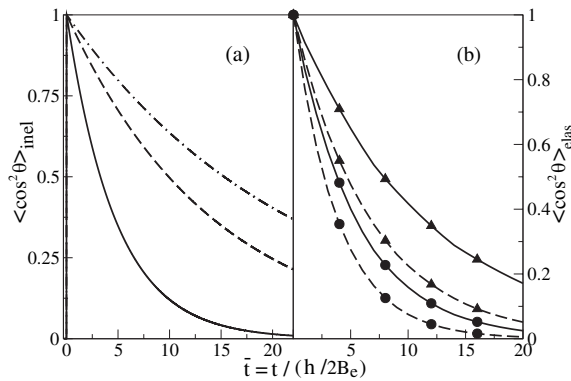


FIG. 2. Normalized measures of the (a) inelastic and (b) elastic collision dynamics as extracted from the observable $\langle \cos^2 \theta \rangle$ for an interaction strength of $\bar{\Omega}_R = 8.73$, illustrating the sensitivity of laser alignment to the dissipative properties of the medium. (a) $\langle \cos^2 \theta \rangle_{\text{inel}}$ vs time for different temperatures: $\bar{T} = kT / B_e = 3.61$ (solid curve), 20 (dashed curve), 36.2 (dot-dashed curve). (b) $\langle \cos^2 \theta \rangle_{\text{elas}}$ for different temperatures: $\bar{T} = 20$ (dashed curve), 36.2 (solid curve), and different temperature dependencies: $T_2 \propto T^{-1.03}$ (circles), $T_2 \propto T^{-0.5}$ (triangles).

along with its two components. The time evolution of $\langle \cos^2 \theta \rangle_p$ (dashed curve and circles), which describes the population, is clearly reproduced by the (observable) baseline of $\langle \cos^2 \theta \rangle$. The time evolution of $\langle \cos^2 \theta \rangle_c$ (dotted curve), which provides the coherences, is reproduced by the (observable) difference curve, $\langle \cos^2 \theta \rangle - \langle \cos^2 \theta \rangle_p$. The dot-dashed curve in Fig. 1, which traces the decay of the coherences, is discussed below. We find that the partitioning of the signal in Eq. (2) translates the experimental observable into a direct probe of the time scales involved in the evolution of the system density matrix.

In Fig. 2 we explore the sensitivity of the experimental observable to the details of the dissipation dynamics. We define independent measures of inelastic and elastic scattering events as the baseline of $\langle \cos^2 \theta \rangle$ and the ratio of the oscillation amplitude (dot-dashed curve in Fig. 1) and the baseline, respectively. The former measure, denoted $\langle \cos^2 \theta \rangle_{\text{inel}}$, provides the evolution of $\langle \cos^2 \theta \rangle_p$ and is sensitive only to inelastic collisions. The latter measure, denoted $\langle \cos^2 \theta \rangle_{\text{elas}}$, traces the ratio of the amplitude of $\langle \cos^2 \theta \rangle_c$ and $\langle \cos^2 \theta \rangle_p$ and reflects solely the dynamics of elastic collisions. Thus, strong-laser-induced alignment signals enable one to decouple and probe within a single measurement the dynamics of population relaxation and decoherence. In the specific case where both the population relaxation and the decoherence can be approximated by a single-exponential decay, we obtain the time constants of population relaxation (T_1), decay of coherence (T_2), and pure dephasing (T_2^*) from the observable $\langle \cos^2 \theta \rangle$ as $\langle \cos^2 \theta \rangle_{\text{inel}} = \langle \cos^2 \theta \rangle_p \propto e^{-t/T_1}$, $\langle \cos^2 \theta \rangle_c \propto e^{-t/T_2} \equiv e^{-t/(T_1+T_2^*)}$, and $\langle \cos^2 \theta \rangle_{\text{elas}} = \langle \cos^2 \theta \rangle_c / \langle \cos^2 \theta \rangle_p \propto e^{-t/T_2^*}$. Our approach, however, is general, rather than restricted to the single-exponential decay limit. [In the specific cases studied here, our analysis indicates single-exponential decay dynamics for the gaseous systems at high temperatures with marked deviations from this limit at low temperatures

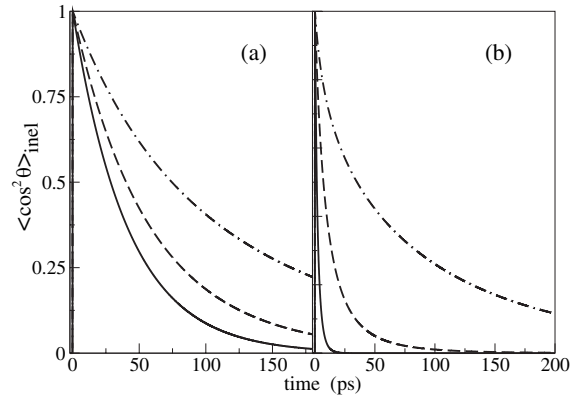


FIG. 3. Intensity dependence of the population relaxation rate for (a) CO/Ar and (b) N_2/H_2O , illustrating the possibility of slowing down the relaxation by the choice of the field parameters: (a) $\bar{\Omega}_R = 2.9$ (solid curve), 291.3 (dashed curve), and 583 (dot-dashed curve). (b) $\bar{\Omega}_R = 2.79$ (solid curve), 279.5 (dashed curve), and 559.5 (dot-dashed curve).

(~ 10 K) as well as for D_2 in liquid Ar.] Figure 2(a) shows $\langle \cos^2\theta \rangle_{\text{inel}}$ at different temperatures, where we use the statistical power-exponential gap law (SPEG) [24,25] with the data of [16] to describe the $J \rightarrow J'$ transition rates in Eq. (1). Figure 2(a) shows the decreasing rate of population relaxation with increasing temperature at constant (200 Torr) pressure, an expected effect given the J dependence of the corresponding rates (see, e.g., [16]). More interestingly, Fig. 2(a) illustrates the sensitivity of $\langle \cos^2\theta \rangle_{\text{inel}}$ to small changes in the system parameters. Figure 2(b) provides $\langle \cos^2\theta \rangle_{\text{elas}}$ for two somewhat different temperature dependencies of the decoherence rate and two temperatures. In the calculations shown as solid circles, elastic collision rates have been assumed to have a similar temperature dependence ($T^{-1.03}$) as the inelastic rates within the SPEG model. Such a behavior has been predicted and experimentally observed in N_2 systems [22]. In the calculations shown as triangles, elastic collision rates scale as $T^{-0.5}$. The sensitivity of $\langle \cos^2\theta \rangle_{\text{elas}}$ to the extent of elastic collisions is evident.

In Fig. 3 we examine the possibility of suppressing the decay and decoherence processes in realistic molecular systems by choosing the pulse parameters so as to shift the center of the wave packet to larger J values. Given the highly nonlinear nature of rotational spectra ($E_J - E_{J-2} \propto J$), one expects the rate of rotationally inelastic collisions to decay rapidly with J . This expectation is confirmed by scattering calculations and experimental measurements, although the extent of J dependence varies from system to system. (For the extensively studied CO/Ar system the line-broadening coefficients vary by less than a factor of 2 as J increases from 0 to 16 [16], whereas for H_2 immersed in dense supercritical Ar the computed population relaxation lifetime increases by a factor of 10 as J increases from 2 to 5 and continues to grow with J [26].) A nontrivial question is the feasibility of utilizing this favorable J dependence to increase the lifetime of aligned wave packets by properly structuring the rotational wave packet under realistic intensities.

Figure 3 illustrates the intensity dependence of the population relaxation rate for two systems that exhibit widely differing relaxation dynamics, CO/Ar [Fig. 3(a)], for which the J dependence of the rate is weak, and N_2/H_2O [Fig. 3(b)] for which it is relatively strong. The rapid slowdown of the population decay with increasing intensity suggests a variety of interesting applications of short-pulse-induced alignment in dissipative media. Clearly, the peak intensity is a rather primitive handle on the rotational content of the wave packet. It would be desirable for future theoretical work to explore more efficient means of structuring the rotational wave packet so as to minimize decay and decoherence. In a forthcoming publication we examine the applicability of optimal control theory (already successfully applied to optimize orientation in isolated molecules [7]) to that end.

In summary, we extended the theory of postpulse alignment induced by short intense pulses to dissipative media

within a density matrix formalism. Our results illustrate the potential of intense laser alignment both as a coherence spectroscopy with unique sensitivity to molecule-bath interactions, and as a control tool of molecular dynamics in dissipative environments.

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