

Time-dependent depolarization of aligned D_2 caused by hyperfine coupling

Nate C.-M. Bartlett,^a Justinas Jankunas,^a Richard N. Zare*^a and John A. Harrison^b

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Molecular deuterium is prepared in the $J = 2, M = 0$ sublevel of $\nu = 1$ by stimulated Raman pumping of the $\nu = 0$ $S(0)$ line. Following optical excitation, the degree of alignment of the rotational angular momentum J oscillates in time caused by the coupling of J to the total nuclear spin angular momentum I_T . This coupling is of two kinds, the interaction of J with the magnetic moments and the quadrupole fields of the two $I = 1$ deuterium nuclei. The alignment is monitored *via* the $O(2)$ line of the $E, F^1\Sigma_g^+ - X^1\Sigma_g^+ (0,1)$ band using $[2+1]$ resonance enhanced multiphoton ionization for pump–probe delays from 0 to 20 μs . Using the hyperfine coupling constants found previously for the $\nu = 0$ state (R. F. Code and N. F. Ramsey, *Phys. Rev. A*, 1971, 4, 1945), we are able to fit the time dependence essentially within our experimental error, but this requires that the presence of both $I_T = 0$ and $I_T = 2$ nuclear spin states for this *o*-deuterium level is properly weighted and taken into account.

Introduction

The preparation of oriented and aligned molecules is important in a wide range of applications which has led to the development of several experimental techniques for this purpose.^{1–4} Previously, we investigated⁵ the time-dependent alignment of the HD ($\nu = 1, J = 2, M = 0$) level under collision-free conditions and were able to follow how the alignment varied between 0 and 13 μs . This study is an extension of that work to the D_2 molecule in which we study the same level but up to 20 μs . This extension, however, is not totally straightforward because of the homonuclear nature of the D_2 molecule, which causes *ortho* and *para* modifications in which the *ortho* levels have even J and total nuclear spin $I_T = 0, 2$ and the *para* levels have odd J and total nuclear spin $I_T = 1$.

While aligned reagents are typically prepared for their use in a subsequent process, perhaps most commonly as targets in scattering experiments, they are interesting in their own right. The nuclei and electrons of a rotating molecule produce opposing current loops of different magnitude, thereby giving rise to a net magnetic field. It is the interaction of the electronic and nuclear spins with this magnetic field that leads in part to the fine and hyperfine structure of a molecule's rotational energy level spectrum, respectively. In addition, $I = 1$ nuclei are not spherical but instead possess a quadrupole charge distribution, which also couples to the rotational angular momentum of the molecule. The optical pumping process that aligns or orients the rotational angular momentum J leaves unchanged any “hidden” angular momenta, those which are invisible to the electric dipole allowed transition of which the electronic spin angular momenta S and nuclear spin angular

momenta I are examples. Following optical excitation J recouples to S and I , which causes oscillations of its alignment in time. These phenomena, known as fine and hyperfine depolarization, respectively, are perhaps most easily understood pictorially with a classical angular momentum vector model. For the following discussion we concentrate only on hyperfine depolarization (thus omitting the electronic spin angular momentum S) noting that ground-state D_2 is in a singlet state but emphasize that when $S \neq 0$ it must also be included.

Consider the simple case of a rotating homonuclear diatomic molecule with rotational angular momentum J and

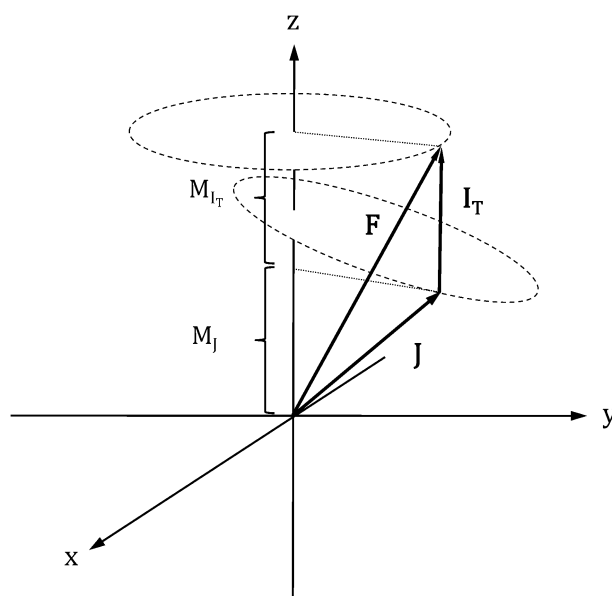


Fig. 1 Illustration of the vector model of the angular momentum coupling of J and I_T . The precession of J about F leads to time dependence of its spatial direction.

^a Department of Chemistry, Stanford University, Stanford, California 94305-5080, USA. E-mail: zare@stanford.edu

^b Institute of Natural Sciences, Massey University, Private Bag 102 904, North Shore Mail Centre, Auckland, New Zealand

total nuclear spin angular momentum I_T . The coupling of J and I_T is represented classically by their vector addition to form the total angular momentum F about which J and I_T precess (Fig. 1). The precession of J about F causes time-dependent behavior of its spatial direction, which is most pronounced when J and I_T are similar in magnitude.

We monitor the degree of rotational alignment of deuterium molecules prepared in the $D_2(\nu = 1, J = 2, M = 0)$ state under collision-free conditions for pump–probe delays of up to 20 μs . To our knowledge this is the first study of its type for D_2 and is the longest amount of time hyperfine depolarization has been measured for any molecular system. In what follows, we present the measurements we obtained for the time variation of the alignment, we develop the theory to describe this process, and we discuss how well the theory is able to match the experimental findings.

Experimental

In this section we present only the techniques relevant to the current study, which builds on previous work.^{5,6} Fig. 2 presents the experimental setup. In brief, D_2 (Cambridge Isotopes, 99.8% purity) was diluted to 15% in Kr and supersonically expanded into the extraction region of a Wiley–McLaren time-of-flight (TOF) spectrometer through a pulsed valve (General Valve Series 9), backed by a total pressure maintained at 1000 Torr. This produces an expansion with nearly all $D_2(\nu = 0)$ in low rotational levels. Some of the molecules in the $D_2(\nu = 0, J = 0)$ level are then pumped *via* the two-photon stimulated Raman pumping (SRP) $S(0)$ transition using linearly polarized light to the $D_2(\nu = 1, J = 2, M = 0)$ state, producing an aligned sample. This excited-state D_2 was subsequently ionized state-selectively using $[2+1]$ REMPI *via* the $O(2)$ line of the $E, F \ ^1\Sigma_g^+ - X \ ^1\Sigma_g^+ (0,1)$ band following a variable pump–probe time delay produced by a digital delay generator, thereby monitoring the time dependence of the alignment. The electric vector of the ionization laser was also linearly polarized and was alternated between being parallel and perpendicular to those of the SRP

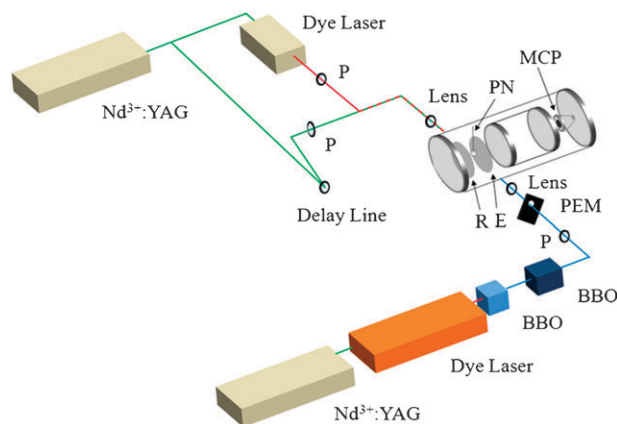


Fig. 2 Schematic diagram of the experimental apparatus. Abbreviations are as follows: BBO = β -barium borate crystal; E = extractor grid; MCP = microchannel plates; PEM = photoelastic modulator; P = linear polarizer; PN = pulsed nozzle; R = repeller plate.

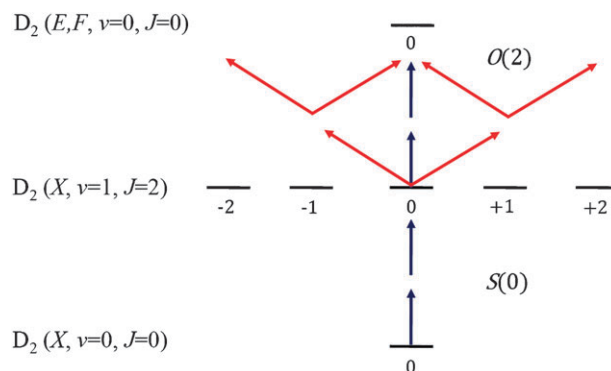


Fig. 3 SRP and REMPI schemes used to prepare and detect $D_2(\nu = 1, J = 2, M = 0)$ from $D_2(\nu = 0, J = 0)$ using linearly polarized light. Vertical and angled arrows represent the electric field vector of the probe laser parallel and perpendicular to the pump lasers (also vertical arrows).

lasers (which are parallel to each other) on a shot-to-shot basis by passing it through a photo-elastic modulator (Hinds PEM-80). The spectroscopic scheme is displayed in Fig. 3. The D_2^+ ions are extracted orthogonal to their initial direction of motion through a slit into a field-free drift tube and the ion current is recorded by a pair of microchannel plates. The two ion current signals are hereafter referred to as I_{\parallel} and I_{\perp} corresponding to the two laser geometries. The velocity of the molecular beam and the size of the extractor slit place a physical constraint on the largest pump–probe delay that can be achieved. We have doubled the length of this slit for the current study which has allowed for data collection for pump–probe delays of up to 20 μs . To achieve the longest pump–probe delay possible, the SRP lasers are focused near the top of the slit while the probe laser focus position is varied along the direction of motion of the molecular beam as the delay is increased.

The two wavelengths involved in the SRP process are commonly referred to as the pump and Stokes wavelengths. For a pump beam of $\lambda = 532$ nm, the Stokes beam is tuned to $\lambda = 639.927$ nm for the SRP $S(0)$ transition. The pump beam is produced by the second harmonic of an injection-seeded $\text{Nd}^{3+}:\text{YAG}$ laser (Continuum PL9020) and the Stokes beam is produced by a dye laser (Continuum ND6000, DCM dye). The $O(2)$ line of the $E, F \ ^1\Sigma_g^+ - X \ ^1\Sigma_g^+ (0,1)$ band occurs at 207.427 nm and is produced by frequency tripling the output of a $\text{Nd}^{3+}:\text{YAG}$ pumped dye laser (Spectra-Physics DCR-2A and Spectra-Physics PDL-3, respectively). The pulsed valve and all lasers operated at 20 Hz and all wavelengths were measured with a wavelength meter (WaveMaster, Coherent).

Results

Fig. 4 displays the ratio of the experimentally measured polarization-dependent ion signals I_{\parallel} and I_{\perp} as a function of pump–probe delays. At time $t = 0$, the value of I_{\parallel}/I_{\perp} is close to 4.0, which has been shown previously to be the expected value for no hyperfine depolarization.⁶ As time increases, this polarization ratio decreases reaching a first minimum at 3.5 μs

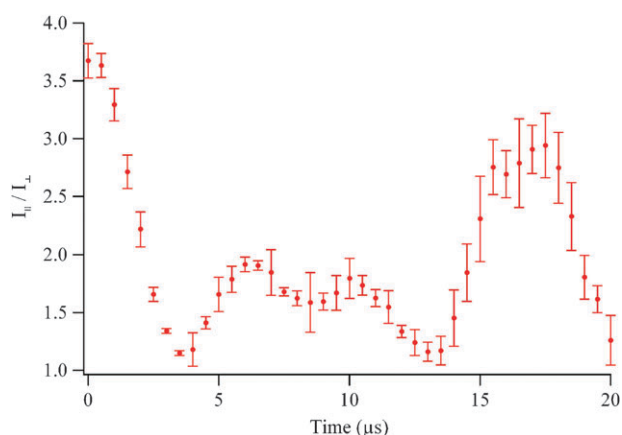


Fig. 4 Experimentally measured time evolution of the $D_2(v = 0, J = 2, M = 0)$ rotational polarization ratio I_{\parallel}/I_{\perp} as a function of SRP-REMPI time delay.

with a value close to $I_{\parallel}/I_{\perp} = 1$, which is the expected value for no alignment. At still later times, the polarization oscillates and rises to a maximum at about $17.5 \mu\text{s}$ before diving once more. The fact that the polarization ratio at such long times is able to reach such a large value gives us confidence that collisional depolarization effects are minor but non-negligible (see Discussion) over the time scale we have investigated.

The error bars in Fig. 4 represent two standard deviations, based on five repeated measurements. Close examination of Fig. 4 shows that the error bars increase with the distance the molecules have traveled before being detected, that is, with pump-probe delay. This result is expected because of the divergence of the molecular beam. Another contributing factor, which is likely the more important, is that at long pump-probe delays the molecules are not extracted along the axis of the detector so that less of them are collected. Nevertheless, the present data present a good test of how well we can describe hyperfine depolarization.

Theory

The spatial distribution of the rotational angular momenta \mathbf{J} of a molecular ensemble may be described either by the $(2J + 1)^2$ density matrix elements $\rho_{MM'}$ or the $(2J + 1)^2$ multipole moments, $A_q^{(k)}(\mathbf{J})$ where $k \leq 2J$ and $-k < q < k$. The two sets of parameters are equivalent and related by¹

$$\rho_{MM'} = \sum_{k,q} \frac{(2k+1)[J(J+1)]^{k/2}}{c(k)\langle \mathbf{J} \parallel \mathbf{J}^{(k)} \parallel \mathbf{J} \rangle} (-1)^{J+q-M'} \times \begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix} A_q^{(k)}(\mathbf{J}) \quad (1)$$

$$A_q^{(k)}(\mathbf{J}) = \frac{c(k)}{\langle \mathbf{J} \parallel \mathbf{J}^2 \parallel \mathbf{J} \rangle^{k/2}} \sum_{M,M'} \rho_{MM'} \langle \mathbf{J} M \parallel \mathbf{J}_q^{(k)} \parallel \mathbf{J} M' \rangle \quad (2)$$

where the $c(k)$ are normalization constants: $c(0) = c(1) = 1$, $c(2) = \sqrt{6}$, $c(3) = \sqrt{5/2}$, and $c(4) = \sqrt{35/8}$. The $A_q^{(k)}(\mathbf{J})$ parameters tend to be more convenient for applications

involving optical excitation and we use them in our description. We define $A_q^{(k)}(\mathbf{J}, t = 0)$ to be the multipole moments of the system at the instant of optical excitation and are calculated through eqn (2). If the optical excitation produces a cylindrically symmetric spatial distribution of \mathbf{J} about some chosen axis, moments with $q \neq 0$ vanish so that only $(2J + 1)$ parameters are needed. Additionally, if linearly polarized light is used in the optical excitation process, only the even rank multipole moments are nonzero.

We make the assumption that the initial spatial distribution of the nuclear spins is random and unaffected by the excitation process. Following excitation, the rotational and nuclear spin angular momenta couple, and this leads to a time-dependent spatial distribution for each. The time dependence of the rotational angular momentum spatial distributions can be expressed in terms of the initial multipole moments $A_q^{(k)}(\mathbf{J}, t = 0)$ multiplied by a perturbation coefficient $G^{(k)}(\mathbf{J}, t)$ such that

$$A_q^{(k)}(\mathbf{J}, t) = A_q^{(k)}(\mathbf{J}, t = 0) G^{(k)}(\mathbf{J}, t) \quad (3)$$

Different angular momentum coupling schemes give rise to different expressions for $G^{(k)}(\mathbf{J}, t)$.

In the following we consider only the case in which the molecule contains two identical nuclei (e.g., H_2 , D_2 , N_2 , C_2H_2) which first couple to give total nuclear spin \mathbf{I}_T . The total nuclear spin \mathbf{I}_T then couples to the rotational angular momentum \mathbf{J} to give the total angular momentum of the system \mathbf{F} , as shown in Fig. 1. The perturbation coefficient for this $|I_T J F\rangle$ coupling scheme has been worked out and is expressed as⁷

$$G^{(k)}(\mathbf{J}, t) = \sum_{F,F'} \frac{(2F+1)(2F'+1)}{(2I_T+1)} \left\{ \begin{matrix} F' & F & k \\ J & J & I_T \end{matrix} \right\}^2 \times \cos \left[\frac{(E_F - E_{F'})t}{h} \right], \quad (4)$$

where the E_F are the energies of the hyperfine levels which result from the coupling of the rotational and nuclear spin angular momenta.

Rutkowski and Zacharias⁸ have used eqn (4) to calculate the depolarization of D_2 for $J = 1-10$. However, this work was followed by a corrigendum⁹ that explains in part why eqn (4) cannot be applied to o - D_2 ($J = \text{even}$). The authors point out that eqn (4) works only for systems whose hyperfine Hamiltonian is diagonal in the $|I_T J F\rangle$ basis and that for o - D_2 the $|I_T = 0, J F = J\rangle$ and $|I_T = 2, J F = J\rangle$ states are coupled, which leads to two off-diagonal elements appearing in the $F = J$ block.^{10,11} They do not however present a perturbation coefficient for o - D_2 . The effect of off-diagonal elements in the Hamiltonian on the perturbation coefficient has been worked out by Altkorn *et al.*¹² but not for the case of *ortho/para* systems. Actually, there is still an additional complication, which is that o - D_2 exists in both the $I_T = 0$ and $I_T = 2$ states with statistical weights of $1/6$ and $5/6$ respectively. For p - D_2 ($J = \text{odd}$) only $I_T = 1$ needs to be considered and the calculation of $G^{(k)}(\mathbf{J}, t)$ is straightforward.

After taking both of these factors into account, the perturbation coefficient for $o\text{-D}_2$ is

$$\begin{aligned}
 G^{(k)}(J, t) &= \sum_{I_T, I_T'} W_{I_T} \sum_{\alpha, \alpha', F, F'} \frac{(2F+1)(2F'+1)}{(2I_T+1)} \left\{ \begin{matrix} F' & F & k \\ J & J & I_T \end{matrix} \right\}^2 \\
 &\quad \times \cos \left[\frac{(E_{\alpha, F} - E_{\alpha', F'}) t}{h} \right] (C_{I_T, \alpha}^{(F)} C_{I_T, \alpha'}^{(F')*} \delta_{I_T, I_T'})^2 \\
 &= \sum_{I_T} W_{I_T} \sum_{\alpha, \alpha', F, F'} \frac{(2F+1)(2F'+1)}{(2I_T+1)} \left\{ \begin{matrix} F' & F & k \\ J & J & I_T \end{matrix} \right\}^2 \\
 &\quad \times \cos \left[\frac{(E_{\alpha, F} - E_{\alpha', F'}) t}{h} \right] (C_{I_T, \alpha}^{(F)} C_{I_T, \alpha'}^{(F')*})^2
 \end{aligned} \tag{5}$$

where the hyperfine energy levels are now labeled by $E_{\alpha, F}$ and $C_{I_T, \alpha}^{(F)}$ are the expansion coefficients of the $|I_T J F\rangle$ basis. The index α need not be assigned a specific value as its only role is to differentiate the eigenvalues and assign to each the appropriate eigenvector. Additionally, W_{I_T} is the weighting factor for the different values of I_T . Note that the sum over I_T in eqn (5) should be performed only over $I_T = 0$ and $I_T = 2$. The inclusion of the Kronecker delta $\delta_{I_T, I_T'}$ in the first line of eqn (5) reminds us that the $I_T = 0$ and $I_T = 2$ contributions are calculated independently, even though the $F = 2$ hyperfine level involves their superposition. Because the optical excitation process does not affect the total nuclear spin angular momentum, this implies that the molecules are at all times (before and after being pumped) in $I_T = 0$ or $I_T = 2$ (and in their 1 : 5 statistical ratios) but not a superposition of both. Finally, note that $G^{(k)}(J, t = 0) = 1$, as it must, which can be easily shown using the orthogonality properties of the $6J$ symbols.

Next, we outline the calculation of the perturbation coefficients $G^{(k)}(J, t)$ for $\text{D}_2(J = 2)$ and use the results to compare our experimental data to theory. This requires a calculation of the eigenvalues and eigenvectors of the D_2 hyperfine Hamiltonian, which in the absence of external fields is given by^{10,11}

$$\begin{aligned}
 \frac{H}{h} &= c_d \left(\frac{I_T(I_T+1) + J(J+1) - F(F+1)}{2} \right) \\
 &\quad - 15\sqrt{30}d'_M (-1)^{F+I_T+J} (2J+1) \sqrt{2I_T+1} \sqrt{2I_T'+1} \\
 &\quad \times \begin{pmatrix} J & 2 & J \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} F & J & I_T' \\ 2 & I_T & J \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ I_T' & I_T & 2 \end{Bmatrix} \\
 &\quad + \frac{2\text{eqQ}}{4h} (-1)^{2I_T+J+F+1} \\
 &\quad \times \left(\frac{30(2I_T+1)(2I_T'+1)J(J+1)(2J+1)}{(2J-1)(2J+3)} \right)^{1/2} \\
 &\quad \times \begin{Bmatrix} 1 & I_T' & 1 \\ I_T & 1 & 2 \end{Bmatrix} \begin{Bmatrix} F & J & I_T' \\ 2 & I_T & J \end{Bmatrix},
 \end{aligned} \tag{6}$$

where c_d is the spin-rotational interaction constant, d'_M is the nuclear spin-nuclear spin magnetic interaction constant, and eqQ is the quadrupole interaction constant. For $\text{D}_2(\nu = 0, J = 2)$ these hyperfine interaction constants have been experimentally determined by Code and Ramsey¹⁰ to have the values $c_d = 8.723$ kHz, $d'_M = 2.72$ kHz, and eqQ = 223.38 kHz. Although we have produced $\text{D}_2(\nu = 1, J = 2)$ in the present study, we use the ground-state constants in the calculation of $G^{(k)}(J, t)$ because the excited state constants have not to our knowledge been determined. We found previously for the HD molecule that our experiment was not sensitive enough to distinguish between the ground and first excited vibrational state hyperfine constants, that is, the use of the ground-state constants in the calculation of $G^{(k)}(J, t)$ produced so good a match between theory and experiment that it was not possible to use the experimental measurements to demonstrate how the hyperfine constants differ in going from $\nu = 0$ to $\nu = 1$.

The matrix elements of the Hamiltonian may be readily evaluated using eqn (6) and are displayed in Tables II and IV of ref. 10. In particular, note in Table II of the same reference the off-diagonal matrix element $\langle 022|H/h|222\rangle$. It is this off-diagonal element that necessitates the inclusion of the $C_{I_T, \alpha}^{(F)}$ eigenvector coefficients in eqn (5). The $F = J$ block of the $o\text{-D}_2$ hyperfine Hamiltonian will in general not be diagonal in the $|I_T J F\rangle$ basis. Finally, diagonalization of the Hamiltonian yields the eigenenergies $E_{\alpha, F}$ and coefficients $C_{I_T, \alpha}^{(F)}$ which allow for the evaluation of the perturbation coefficients.

In Fig. 5 we display again the ratio of the experimentally measured polarization-dependent ion signals I_{\parallel} and I_{\perp} as a function of pump-probe delays but against a calculated ratio based on eqn (7) and (8) described below. These two-photon ionization signal intensities may be expressed in terms of a multipole expansion⁵

$$I_{\parallel} = I_0[1 + s_2 A_0^{(2)}(t=0)G^{(2)}(t) + s_4 A_0^{(4)}(t=0)G^{(4)}(t)] \tag{7}$$

$$I_{\perp} = I_0[1 - \frac{1}{2}s_2 A_0^{(2)}(t=0)G^{(2)}(t) + \frac{3}{8}s_4 A_0^{(4)}(t=0)G^{(4)}(t)] \tag{8}$$

The $A_0^{(k)}(t=0)$ depend on the values of J and M of the prepared state, while the s_k (the $[2+1]$ REMPI sensitivities to

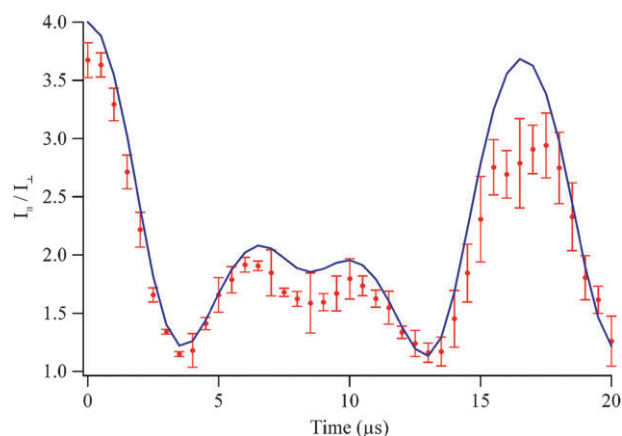


Fig. 5 Experimentally measured time evolution of the $\text{D}_2(\nu = 0, J = 2, M = 0)$ rotational polarization ratio I_{\parallel}/I_{\perp} versus the calculated time evolution based on eqn (7) and (8) as a function of SRP-REMPI time delay.

the $A_0^{(k)}$ depend on the initial and final values of J in the REMPI step and the polarization of the light. For the $O(2)$ line of the $E,F\ ^1\Sigma_g^+ - X\ ^1\Sigma_g^+ (0,1)$ band using linearly polarized light and assuming 100% population in the $M_J = 0$ sublevel, $s_2 = -10/7$, $s_4 = 72/7$, $A_0^{(2)}(t = 0) = -1$ and $A_0^{(4)}(t = 0) = 1/4$. Comparison of the experimental data with the theoretical calculation shows good agreement but there is a clear systematic experimental error which causes the ratio I_{\parallel}/I_{\perp} to be smaller than the predicted value at all times. As will be discussed, this discrepancy arises from imperfect polarization in the REMPI probe and from a small amount of collisional depolarization.

Discussion

As shown in Fig. 5, theory is able to show the same types of polarization oscillations with time as found experimentally, but the experimental values are too low. We believe that these deviations are caused primarily by imperfections in our polarization process for detection of the target molecule and by a small amount of collisional depolarization. The former should be the only factor at time $t = 0$ when hyperfine and collisional depolarization have not had sufficient time to take effect. The polarization purity of the detection laser and collisional depolarization can be accounted for in the theoretical signal which then takes the form

$$\text{Signal}(t) = [xI_{\parallel} + (1-x)I_{\perp}]/[(1-x)I_{\parallel} + xI_{\perp}]\exp(-\alpha t) \quad (9)$$

where x and $(1-x)$ represent the fractions of the s and p component of linearly polarized light that emerges from the photo-elastic modulator and α represents the collisional depolarization coefficient. We find that a value of $x = 0.977$ locks the experimental data to the theory at $t = 0$, and $\alpha = 3 \times 10^3 \text{ s}^{-1}$ provides the best overall fit. The resulting corrected theory is displayed in Fig. 6, where it is compared to the experimental measurements. The agreement is nearly everywhere within the error bars of the experimental measurements.

Other factors that we considered as possible contributions to the discrepancy between the experiment and theory were the

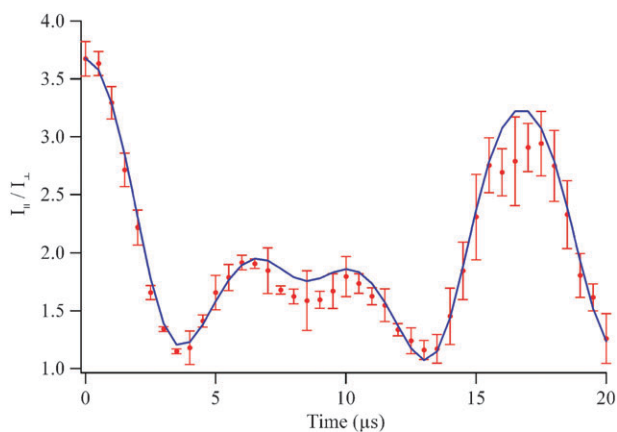


Fig. 6 Experimentally measured time evolution of the $D_2(v = 0, J = 2, M = 0)$ rotational polarization ratio I_{\parallel}/I_{\perp} versus the corrected time evolution calculated from eqn (9) as a function of SRP-REMPI time delay.

polarization purity of the SRP lasers, the relative angle between the electric field vectors of the SRP lasers and the probe laser, and the angle between the three laser beams that arise when the beams are not exactly counter-propagating. The polarization purity of the Nd^{3+} :YAG and dye lasers outputs are in excess of 98% and after each laser beam passes through a linear polarizer the polarizations are well in excess of 99%. Furthermore, the dependence of the experimental signal on the relative angle between the SRP and probe lasers is very weak for small angle deviations as it is a function of $P_2[\cos(\theta)]$ and $P_4[\cos(\theta)]$. Finally, we find that given the experimental geometries used, the largest angle formed by the SRP and probe laser beams is approximately 2° ; thus, there should be almost no change in the apparent M -state distribution as detected by the probe laser. Consequently, these other contributions are considered to make a negligible change.

The agreement between the experimental data and the theoretical predictions is both gratifying and disappointing. We are pleased that we have sufficient command over the experimental variables and sufficient understanding of the theory to make such a close match. We are also disappointed in that we are forced to conclude that our experimental sensitivity is not great enough to observe the difference in magnitude between the hyperfine constants c_d , d'_M , and eqQ of the ground and first vibrational state of D_2 . We had reached the same conclusion in our study of HD^5 but thought that the study of D_2 with a more complicated hyperfine structure and for a longer period of observation time might be more revealing. Our results do allow us to estimate a difference of no greater than 5% for the excited state hyperfine constants c_d and d'_M , and no greater than 1–2% for eqQ, as compared to the ground state. It is possible that this technique could be extended to longer observation times, which would provide information on the change of the hyperfine coupling constants with vibration, but this would require a significant increase in the molecular beam flight path between the point of preparation and detection.

Acknowledgements

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