Nuclear-spin-polarization dynamics of H_2, D_2, and HD molecules in magnetic fields

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We study the polarization dynamics of the molecular rotation and the nuclear spin in the presence of magnetic fields, in the hydrogen isotope molecules, H_2, D_2, and HD. If only the rotational or the nuclear angular momentum is polarized, polarization is transferred from one to the other and back in a oscillatory fashion, due to hyperfine quantum beats. Application of magnetic fields is shown to increase the frequencies of these oscillations and reduce their amplitude so that the polarization exchange can be strongly suppressed. We derive the time-averaged polarization as a function of the (static) magnetic field. Finally, we show, using continuous lasers, molecular beams, and static magnetic fields, that the molecular rotation polarization can be transferred and maintained in the nuclear spin, providing highly nuclear-spin-polarized molecules.

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I. INTRODUCTION

Preparation and manipulation of nuclear-spin-polarized (i.e., hyperpolarized) atomic and molecular samples can be crucial for several scientific and technological fields such as NMR and magnetic resonance imaging (MRI) [1,2], particle physics [3], nuclear fusion [4–6], chemistry [7], and quantum computation [8].

Preparation of the hyperpolarized samples can be achieved with various methods, and the choice depends on the atomic or molecular species to be polarized as well as their thermodynamic phase. Noble-gas atoms can be hyperpolarized in the gas phase using spin-exchange optical pumping (SEOP) [9]. Hyperpolarized molecules in the liquid or solid state can be prepared using dynamic nuclear polarization (DNP) [10]. Hyperpolarized molecules of hydrogen isotopes (e.g., H_2, HD, D_2, and DT) in the gas phase can be produced by Stern-Gerlach spin separation [11], recombination of spin-polarized atoms at surfaces [12,13], and by transferring polarization from molecular rotation to nuclear spin [14–16].

When spin-polarized gas-phase atoms are prepared in high densities, most will recombine into molecules. In this case, the polarization will be transferred to the molecular rotation and back to the nuclear spin, in a harmonic fashion, due to the hyperfine interaction [17]. The molecular rotational polarization is sensitive to collisions with other, unpolarized particles or the walls of the experimental chamber. However, this polarization exchange between the nuclear spin and the molecular rotation can be avoided, to a large extent, by using a strong magnetic field which effectively decouples the nuclear and rotational angular momenta. In this way, the nuclear spins, once polarized, can be isolated from the easily depolarized molecular rotation. Furthermore, the hyperpolarized molecules can be trapped (for example, using cryogenic methods) and their polarization can be maintained for large periods of time using strong magnetic fields [18].

When an atomic or molecular beam is employed for the preparation of the hyperpolarized sample (for example, using laser excitation, magnetic "Stern-Gerlach" methods, or recombination at surfaces) we propose that the sample can be subsequently stored by passing the polarized sample rapidly from zero (or low) magnetic field to a high magnetic field. Therefore, to model accurately the polarization dynamics during this process, the effect of the time-dependent magnetic field upon depolarization has to be known.

In this article, we describe the polarization dynamics of hydrogen isotope molecules, H_2, HD, and D_2, in the presence of (time-dependent) magnetic fields for the $J = 1$ rotational state. We will show how the modified depolarization dynamics can be taken into account to design experiments involving molecular-beam preparation of hyperpolarized molecules and to store in strong magnetic fields.

II. THEORY

The polarization dynamics of molecular rotation J due to the hyperfine interaction can be modeled using the $A_q^{(k)}(J)$ multipole moments and the time-dependent *depolarization* coefficients $G^{(k)}(J)$ [17]. The corresponding time-dependent *polarization* coefficients $H^{(k)}(I_{1,2})$ that describe the polarizations of the nuclear spins I_1 and I_2 have been produced in the hierarchical approximation in Ref. [19], while the nonhierarchical description has been given in [20]. The expectation values of the angular momentum projections $\langle m \rangle$ can be evaluated by calculating the elements of the density matrix using

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

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The calculation of the time dependence of the multipole moments $A_q^{(k)}(J)$ is done in the total angular momentum basis $F = I + J$, in which the Hamiltonian is diagonalized, as shown in [21]. However, the total angular momentum quantum number F is conserved only in the absence of magnetic field. In the presence of magnetic fields, F is no longer a good quantum number and the aforementioned diagonalization cannot be performed.

Alternatively, the depolarization dynamics can be simulated solving the Schrödinger equation. The hyperfine Hamiltonians for the H_2, HD, and D_2 have been measured by Ramsey and co-workers and they are given in frequency units, i.e., $H = \frac{\mathcal{H}}{h}$ [22,23]. The Hamiltonian is evaluated in the angular momenta projection representation $|m_J, m_I\rangle$ for H_2 and D_2 ($I_{\text{tot}} = 1$), or $|m_J, m_{I_1}, m_{I_2}\rangle$ for HD. One way to obtain the temporal behavior of these states is to first diagonalize the Hamiltonian and then solve Schrödinger's equation. Thus, after diagonalizing, the Hamiltonian is written as $H = S\Lambda S^{-1}$, where S is the eigenvector matrix (i.e., the columns of S are the Hamiltonian's eigenvectors), S^{-1} is its inverse, and Λ is a diagonal matrix with the eigenvalues of H along its diagonal.

The characteristic polynomials involved in obtaining the eigenvectors and eigenvalues for H_2, D_2, and HD molecules, are of order 9 and 18. According to Abel-Ruffini theorem, polynomials of order 5 or larger cannot be solved analytically; thus in all calculations hereafter, the diagonalizations are performed numerically. Using the Schrödinger equation, $\hat{H}\,|\psi\rangle_t = \frac{i}{2\pi}\frac{\partial}{\partial t}\,|\psi\rangle_t$, the solution is $|\psi\rangle_t = Se^{-2\pi i\Lambda t}S^{-1}|\psi\rangle_0$, where $|\psi\rangle_0$ is the initial state at $t = 0$. Below we give the formulas for the average value of the angular momentum projection $\langle m\rangle$. We describe a situation where the system is initially prepared in the $\langle m_J\rangle = 1$ state, i.e., the molecular rotation is oriented. For H_2 and D_2 ($I_{\text{tot}} = 1$):

$$\langle m_I\rangle = \frac{\sum_{m_{I'},m_J,m_{I''}=-1}^{1} m_{I''}\,|\,{}_0\langle +1, m_{I'}|m_J, m_{I''}\rangle_t\,|^2}{\sum_{m_{I'},m_J,m_{I''}=-1}^{1}\,|\,{}_0\langle +1, m_{I'}|m_J, m_{I''}\rangle_t\,|^2} \tag{2}$$

and

$$\langle m_J\rangle = \frac{\sum_{m_I,m_{J'},m_{I'}=-1}^{1} m_{J'}\,|\,{}_0\langle +1, m_I|m_{J'}, m_{I'}\rangle_t\,|^2}{\sum_{m_I,m_{J'},m_{I'}=-1}^{1}|\,{}_0\langle +1, m_I|m_{J'}, m_{I'}\rangle_t\,|^2}. \tag{3}$$

For HD:

$$\langle m_{I_2}\rangle = \frac{\sum_{m_{I_1},m_J,m_{I_1'}=-1,m_{I_2'},m_{I_2''}=-1/2}^{m_{I_1},m_J,m_{I_1'}=1,m_{I_2'},m_{I_2''}=1/2} m_{I_2''}\left|\,{}_0\big\langle +1, m_{I_1}, m_{I_2'}\big|m_J, m_{I_1'}, m_{I_2''}\big\rangle_t\,\right|^2}{\sum_{m_{I_1},m_J,m_{I_1'}=-1,m_{I_2'},m_{I_2''}=-1/2}^{m_{I_1},m_J,m_{I_1'}=1,m_{I_2'},m_{I_2''}=1/2}\left|\,{}_0\big\langle +1, m_{I_1}, m_{I_2'}\big|m_J, m_{I_1'}, m_{I_2''}\big\rangle_t\,\right|^2}, \tag{4}$$

$$\langle m_{I_1}\rangle = \frac{\sum_{m_{I_1'},m_J,m_{I_1''}=-1,m_{I_2},m_{I_2'}=-1/2}^{m_{I_1'},m_J,m_{I_1''}=1,m_{I_2},m_{I_2'}=1/2} m_{I_1''}\left|\,{}_0\big\langle +1, m_{I_1'}, m_{I_2}\big|m_J, m_{I_1''}, m_{I_2'}\big\rangle_t\,\right|^2}{\sum_{m_{I_1'},m_J,m_{I_1''}=-1,m_{I_2},m_{I_2'}=-1/2}^{m_{I_1'},m_J,m_{I_1''}=1,m_{I_2},m_{I_2'}=1/2}\left|\,{}_0\big\langle +1, m_{I_1'}, m_{I_2}\big|m_J, m_{I_1''}, m_{I_2'}\big\rangle_t\,\right|^2}, \tag{5}$$

$$\langle m_J\rangle = \frac{\sum_{m_{I_1},m_{J'},m_{I_1'}=-1,m_{I_2},m_{I_2'}=-1/2}^{m_{I_1},m_{J'},m_{I_1'}=1,m_{I_2},m_{I_2'}=1/2} m_{J'}\left|\,{}_0\big\langle +1, m_{I_1}, m_{I_2}\big|m_{J'}, m_{I_1'}, m_{I_2'}\big\rangle_t\,\right|^2}{\sum_{m_{I_1},m_{J'},m_{I_1'}=-1,m_{I_2},m_{I_2'}=-1/2}^{m_{I_1},m_{J'},m_{I_1'}=1,m_{I_2},m_{I_2'}=1/2}\left|\,{}_0\big\langle +1, m_{I_1}, m_{I_2}\big|m_{J'}, m_{I_1'}, m_{I_2'}\big\rangle_t\,\right|^2}. \tag{6}$$

The average polarization is defined as

$$\langle m\rangle_{\text{avg}} = \lim_{T\to\infty}\frac{1}{T}\int_0^T \langle m\rangle\, dt. \tag{7}$$

III. RESULTS AND DISCUSSION

Since the hyperfine polarization transfer from the molecular rotation J to the nuclear spin I is maximized when the values of J and I are close, we limit our studies to cases where $J = I = 1$ [17]. Our results (in the absence of magnetic field) for the H_2 and D_2 molecules agree with the angular momentum algebra results [19,24] and the experimental study in the case of the HD molecule [15].

A. Polarization dynamics of H_2, $I = 1$ molecules in magnetic fields

The nuclear spins of the H_2 molecule ($I = \frac{1}{2}$) form the *ortho*-H_2 ($I_{\text{tot}} = 1$) and *para*-H_2 ($I_{\text{tot}} = 0$) states, which couple to even and odd rotational angular momentum states, respectively. The *para*-H_2 molecules do not exhibit hyperfine depolarization of the rotational angular momentum as $I_{\text{tot}} = 0$. Thus, in the following, we need to consider only hyperfine depolarization in *ortho*-H_2, and we do so for the first rotational state $J = 1$.

The Hamiltonian for a homonuclear ${}^1\Sigma$ diatomic molecule in a magnetic field $\vec{B}$ is [22]

$$\begin{aligned}\mathcal{H}/h = {} & -(1-\sigma_i(\vec{J}))a\vec{I}\cdot\frac{\vec{B}}{B} - (1-\sigma_J(\vec{J}))b\vec{J}\cdot\frac{\vec{B}}{B} - c\vec{I}\cdot\vec{J} \\ & + \frac{5d}{(2J-1)(2J+3)}[3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}\vec{I}\cdot\vec{J} - \vec{I}^2\vec{J}^2] \\ & - \frac{5f}{3(2J-1)(2J+3)}\left[3\frac{(\vec{J}\cdot\vec{B})^2}{B^2} - \vec{J}^2\right] - g,\end{aligned} \tag{8}$$

where $\vec{I}$ is the total nuclear spin and $\vec{J}$ is the molecular rotational angular momentum (in units of $\hbar$). The first two terms correspond to the interaction of the nuclear spin and molecular rotational angular momentum with the external magnetic field, respectively. The third term describes the spin rotational magnetic interaction. The fourth term provides for the combination of the spin-spin interaction of the two

TABLE I. Values of the several hyperfine Hamiltonian constants. The constants are given in Hertz and the magnetic field in Gauss. The table is adapted from Refs. [22,23].

Constant in Eq. (8)	H_2	D_2	Constant in Eq. (9)	HD
$(1-\sigma_i(1))a$	4258 B	653.6 B	$(1-\sigma_p(1))a_p$	4257.796 B
			$(1-\sigma_d(1))a_d$	653.5832 B
$(1-\sigma_J(1))b$	671.7 B	336.8 B	$(1-\sigma_J(1))b$	505.5870 B
c	113800	8783	c_p	85589
			c_d	13118
d	57680	25240	d_1	17764
			d_2	−22452
f	Negligibly small	Negligibly small	f	$-26.3\times10^{-6}B^2$
–	–	–	δ	43

nuclei with each other together with the interaction of any nuclear electrical quadrupole moment with the variation of the molecular electric field in the vicinity of the nucleus. The last two terms correspond to the diamagnetic interaction of the molecule with the magnetic field. The values of the constants are given in Table I. However, some of the constants are negligibly small, and they are omitted.

When the *ortho*-H_2 molecules are prepared into an *oriented* distribution, i.e., $\langle m_J\rangle = 1$, for example, using laser excitation, and this is done without hyperfine resolution, the rotational angular momentum and the (total) nuclear spin form the total angular momentum states $|F, M_F\rangle$. The partial angular momenta I and J now precess around F. Thus, the initially polarized molecular rotation gets depolarized and the polarization is transferred to the nuclear spin so that the total angular momentum projection M_F is conserved. The polarization of each partial angular momentum oscillates in a harmonic fashion, and the form of this oscillation is called polarization beating. The solid line in Fig. 1(a) shows the polarization beating of the molecular rotation in the absence of magnetic field for the case of H_2 molecules. As we see, the polarization beating is characterized by two oscillations: a slower oscillation with a period of ∼20 μs and an amplitude of ∼0.5, and a faster oscillation with a period of 2 μs and an amplitude of ∼0.25. The dashed and the light gray lines show the depolarization beating in the presence of a magnetic field of 3 and 15 mT, respectively, parallel to the initial orientation of the molecular rotation. We see that only the fast component of the beating remains.

Figure 1(b) shows the average polarization as a function of the magnetic field B. In the absence of magnetic fields, the hyperfine interaction transfers polarization from the molecular rotation to the nuclear spin in a timescale of tens of microseconds. As a result, the time-averaged polarization of both angular momenta is 50%. As the magnetic field increases, the coupling between the molecular rotation and the nuclear spin is reduced, and the two angular momenta are completely decoupled for fields larger than 60 mT. We notice that the average polarization curve is characterized by two areas of different curvature. This can be explained by observing that the two oscillation frequencies are eliminated for different values of the magnetic field. The lower frequency oscillation of the beating is suppressed at 3 mT, but the higher frequency is eliminated at larger magnetic fields. The latter is indicated in Fig. 1(a), where the rotational polarization is plotted for 3 mT (dashed line).

B. Polarization dynamics of D_2, $I = 1$ molecules in magnetic fields

The D_2 molecule contains two nuclei with nuclear spin of 1. Thus, the total nuclear spin takes the values 0, 1, and 2. Here we examine the case where $I_{\text{tot}} = 1$ and $J = 1$. The

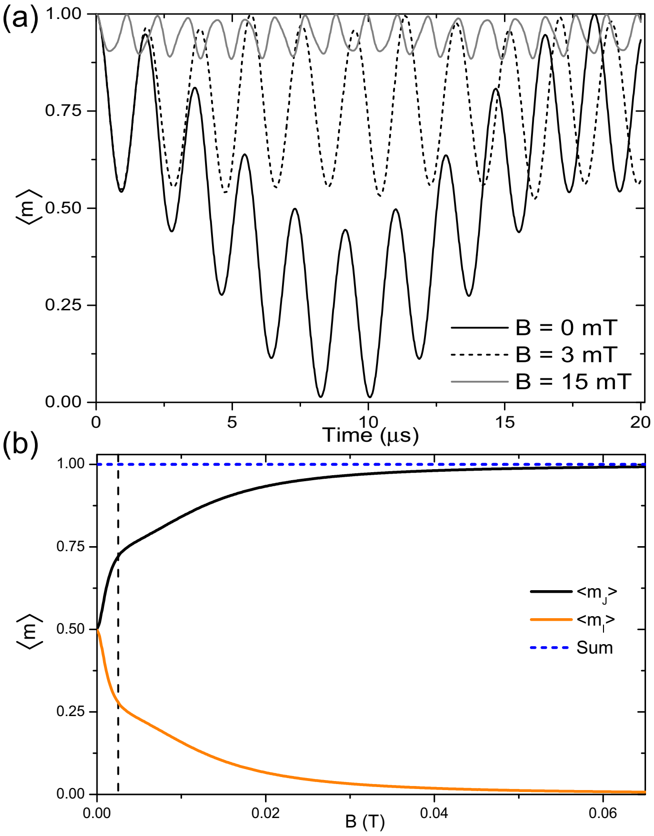

FIG. 1. (a) Polarization beating of the rotational angular momentum for $B = 0$ T (solid line), 3 mT (dashed line), and 15 mT (light gray line). (b) Averaged polarization of the nuclear and rotational angular momentum of an ensemble of H_2 molecules (in the first rotational state $J = 1$) as a function of the magnetic field.

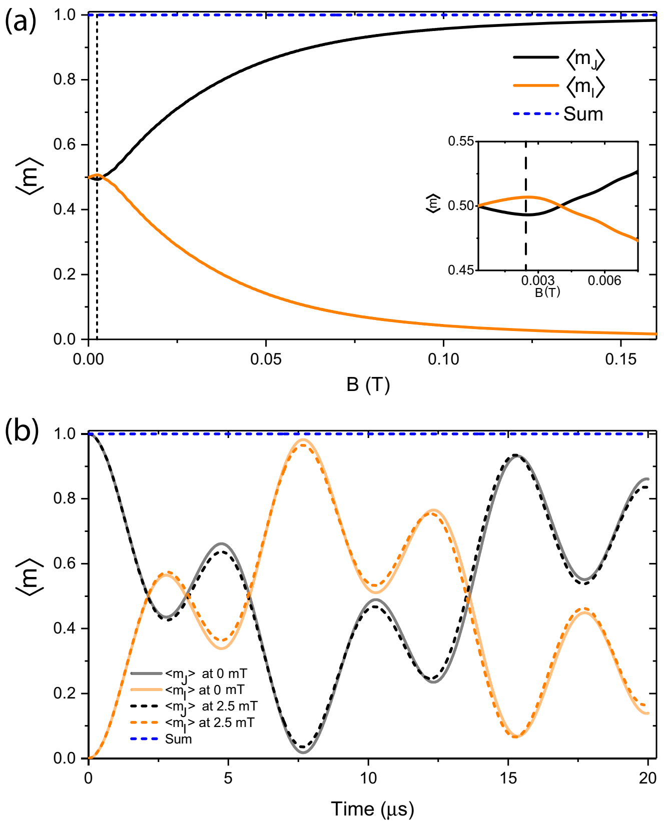

FIG. 2. (a) Polarization of nuclear and rotational angular momenta of D_2 molecule (in the first rotational state $J = 1$) as a function of the magnetic field. (b) Polarization beating of rotational and nuclear angular momenta for $B = 0$ mT (solid line) and 2.5 mT (dashed line).

Hamiltonian that describes the D_2 molecule in magnetic fields is given by Eq. (8) and the constants are given in Table I.

Figure 2(a) shows the nuclear and rotational average polarization as a function of the magnetic field for the D_2 molecules. The nuclear polarization has a small local maximum at 2.5 mT. The polarization beatings for 0 and 2.5 mT are shown in Fig. 2(b). The amplitude of the beating is increased slightly so that the average value is higher compared to the average polarization at 0 T. These counterintuitive dynamics are caused by the interplay between the first and fourth term in Eq. (8). As we explained in the previous section, the first term describes the interaction of the nuclear spins with the external magnetic field and the fourth provides for the combination of the spin-spin interaction of the two nuclei with each other, together with the interaction of any nuclear electrical quadrupole moment with the variation of the molecular electric field in the vicinity of the nucleus.

Figure 3 shows the polarization of molecular rotation J and nuclear spin I as a function of the magnetic field, only that now, the direction of the magnetic field has been chosen to be antiparallel to the initial direction of the molecular rotation orientation. As a result, the relative sign between the first and fourth term in Eq. (8) changed and the phenomenon disappeared.

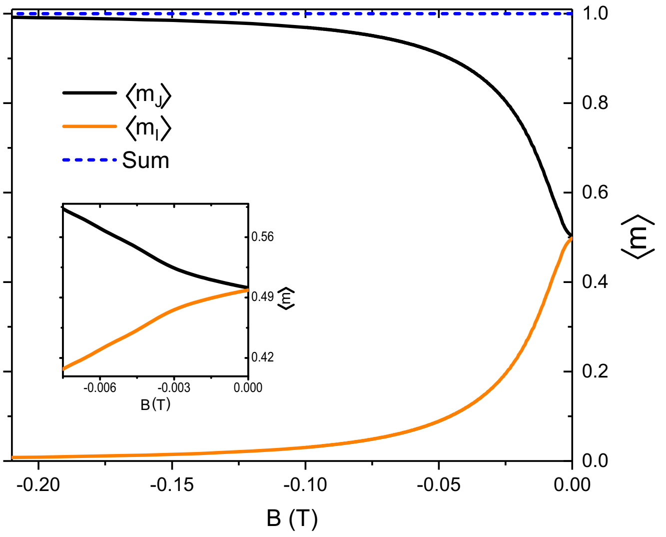

FIG. 3. Polarization of nuclear and rotational angular momenta of D_2 molecule (in the first rotational state $J = 1$) as a function of the magnetic field. Contrary to all other cases, the direction of the magnetic field is here antiparallel to the initial direction of orientation of molecular rotation.

C. Polarization dynamics of HD molecules in magnetic fields

Finally, in the case of the HD molecule, instead of two different angular momenta, we have three, since the nuclear spins (for H and D) are not equal. In Ref. [23], the hyperfine Hamiltonian for the HD molecule is given as

$$\begin{aligned}\mathcal{H}/h = &-(1-\sigma_p(\vec{J}))a_p\vec{I}_2\cdot\frac{\vec{B}}{B}-(1-\sigma_d(\vec{J}))a_d\vec{I}_1\cdot\frac{\vec{B}}{B}\\ &-(1-\sigma_J(\vec{J}))b\vec{J}\cdot\frac{\vec{B}}{B}-c_p\vec{I}_2\cdot\vec{J}-c_d\vec{I}_1\cdot\vec{J}\\ &+\frac{5d_1}{(2J-1)(2J+3)}\left[\frac{3}{2}(\vec{I}_2\cdot\vec{J})(\vec{I}_1\cdot\vec{J})\right.\\ &\left.+\frac{3}{2}(\vec{I}_1\cdot\vec{J})(\vec{I}_2\cdot\vec{J})-\vec{I}_2\cdot\vec{I}_1\vec{J}^2\right]\\ &+\frac{5d_2}{(2J-1)(2J+3)}[3(\vec{I}_1\cdot\vec{J})^2+\frac{3}{2}(\vec{I}_1\cdot\vec{J})-\vec{I}_1^2\vec{J}^2]\\ &-\frac{5f}{3(2J-1)(2J+3)}\left[3\frac{(\vec{J}\cdot\vec{B})^2}{B^2}-\vec{J}^2\right]\\ &-g+\delta\vec{I}_2\cdot\vec{I}_1,\end{aligned} \tag{9}$$

where $\vec{I}_2$ and $\vec{I}_1$ are the nuclear spins for hydrogen and deuterium nuclei, respectively, in units of $\hbar$ and $\vec{J}$ is the molecular rotational angular momentum. The first two terms in Eq. (9) correspond to the interactions of the nuclear spins with the external magnetic fields. The third term includes the interaction of the molecular rotational magnetic moment with the external magnetic fields. The fourth and fifth terms correspond to the spin rotational magnetic interaction. The sixth term provides for the direct spin-spin magnetic interaction between the two nuclei, together with a small contribution from the tensor portion of the electron-coupled nuclear spin-spin interaction. The seventh term involves the interaction of

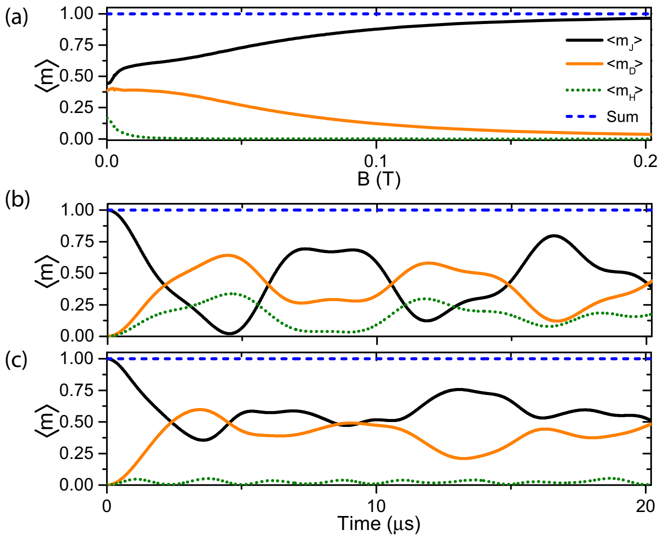

FIG. 4. (a) Polarization of nuclear ($\langle m_D \rangle$, $\langle m_H \rangle$) and rotational ($\langle m_J \rangle$) angular momenta of HD molecule (in the first rotational state $J = 1$) as a function of the magnetic field. Polarization beatings of rotational and nuclear angular momenta for $B = 0$ mT (b) and 10 mT (c).

the electric quadrupole moment of the deuteron. The eighth term arises from the orientation dependence of the diamagnetic susceptibility. The ninth term includes the orientation-independent molecular susceptibility. The last term corresponds to the portion of the electron-coupled nuclear spin-spin interaction that depends only on the nuclear orientation. Here, we examine the first rotational state $J = 1$. The values of the constants are given in Table I.

Figure 4(a) shows the average polarization of the two nuclear angular momenta (deuterium $I_1 = 1$ and hydrogen $I_2 = 1/2$) and rotational angular momentum ($J = 1$) for HD molecules as a function of the magnetic field. In the absence of magnetic fields, the average polarization of the molecular rotation is close to 0.46, with ~0.38 being transferred to the deuterium and ~0.16 to the hydrogen nuclei. As the magnetic field increases, the proton polarization rapidly decreases. As a result of this rapid decoupling of J and I_2, for fields up to 10 mT, the deuteron polarization is enhanced to values larger than 0.38. This is highlighted in Figs. 4(b) and 4(c), where we show the polarization beatings of the angular momenta of HD molecules for $B = 0$ and 10 mT. We see that the maximum polarization of H is reduced from 0.16 to 0.024 when the magnetic field is increased from zero to 10 mT.

D. Modeling the effect of spatially varying magnetic fields: Example with H_2, $I = 1$ molecules

At this point we can employ the previous analysis to model storing hyperpolarized molecules in the presence of magnetic fields. We first present in detail the features of the magnet and subsequently the method to store H_2 molecules with high-nuclear-spin polarization.

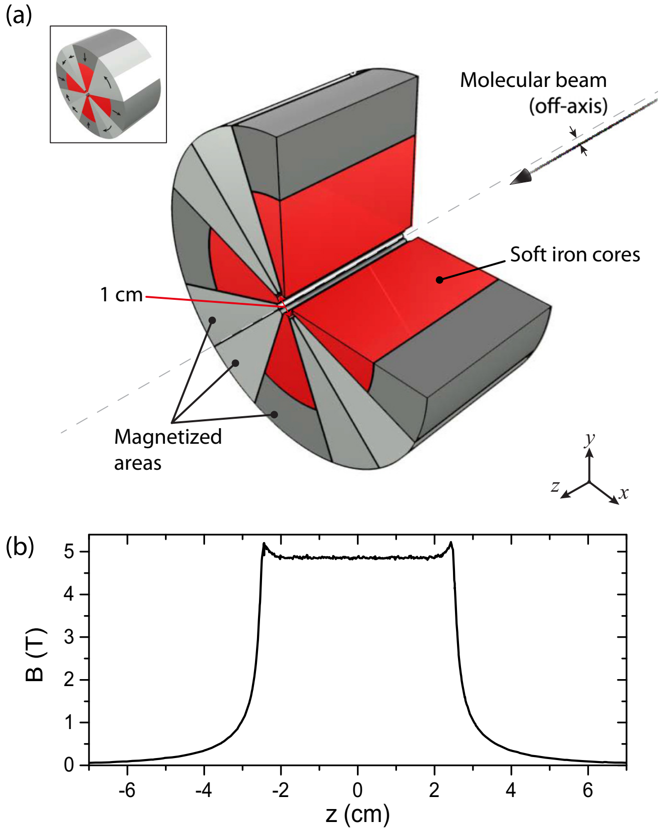

FIG. 5. (a) Scheme of the magnet. (b) The magnetic field as a function of distance from the center of the magnet.

Large magnetic field gradients can be achieved with permanent magnet quadrupoles, which provide higher field strengths and compactness than conventional electromagnets [25–27]. For the purposes of creating the required B_x gradient vertical to the molecular-beam propagation direction z, a quadrupole as shown in Fig. 5(a) was designed and simulated in Comsol. Before we move on with the description of this magnet, we note that this is just an indicative design out of a great multitude of similar possible options, and, as such, it is not optimized to provide the highest possible gradients. Our specific simulated design comprises strongly magnetized areas in the periphery of the largely cylindrical configuration, with magnetizations oriented in the direction indicated by the arrows in Fig. 5(a). Magnetization is on the order of $\sim 10^3$ kA/m in the magnetized areas, consistent with the Hc (coercivity) values for neodymium magnets. The red (interior dark gray) areas in Fig. 5(a) indicate soft-iron cores serving to guide and focus the magnetic field lines to the cylinder bore along which the molecules propagate. The desired B_x gradient is achieved at the entrance of the magnet, as the magnetic field ramps up from zero to its maximum value (see Fig. 6). For the depicted magnetization configuration, the B_x field is higher off of the z axis and towards the positive x axis. For this reason, the molecular beam encounters the B_x gradient by propagating parallel to, but not coinciding with, the z axis and towards the positive x.

As an example of a supposed experiment of preserving nuclear-spin polarization in magnetic fields, we use hydrogen molecules excited in the first rotational state $J = 1$. We can produce hyperpolarized H_2 molecules by orienting the molecular rotation at $t = 0$ and leaving the system to evolve

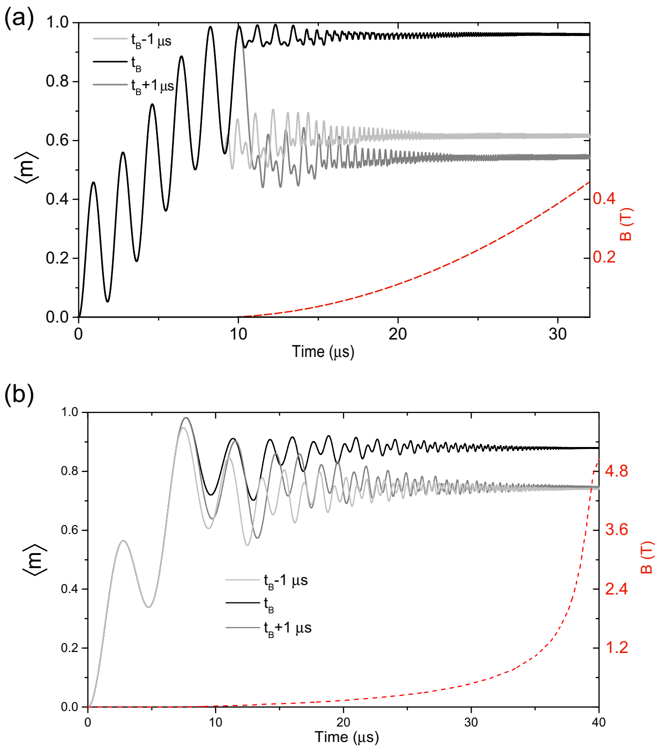

FIG. 6. (a) Polarization dynamics of H_2 molecules with spatially varying magnetic fields. The molecules are rotationally oriented at $t = 0$ and they enter the area of the magnetic field (dashed line) at $t = 10$ (optimum delay), 9, and 11 μs (black, light gray, and dark gray lines). (b) Similar for D_2 molecules; note that in the case of D_2 molecules the optimum delay is $t \sim 7.5$ μs. Red (dashed) line: Time dependence of the field experienced by the molecules traveling in a molecular beam with velocity ~1000 m/s.

in the absence of magnetic fields. The hydrogen molecules are initially prepared in an oriented distribution of their rotational angular momentum, i.e., at $t = 0$, $\langle m_J \rangle = 1$. The hyperfine interaction transfers polarization to the nuclear spin as explained in the previous paragraphs, so that after 10 μs, the average value $\langle m_J \rangle$ is zero and $\langle m_I \rangle$ is 1. At this point the molecules are hyperpolarized and it would be desirable to store them in the presence of a magnetic field so that the hyperpolarization is conserved [18]. In the following paragraph, we show how the timing and the amplitude of the magnetic field can be chosen so that the nuclear-spin polarization can be stored in an optimal way.

Figure 6(a) shows the evolution of the nuclear polarization of the H_2 molecule as a function of time (or, equivalently, of position for a given constant molecule velocity) in the presence of a spatially varying magnetic field, created, for example, by a permanent magnet configuration as in Fig. 5.

Before encountering the magnetic field, the temporal evolution is identical to the one shown in Fig. 1(a). As the molecules fly into the field area, they experience a steep spatial variation of the magnetic field, which decouples the rotational angular momentum from the nuclear spin.

The final value of the polarization strongly depends on the *delay time*, i.e., the timing between the initiation of the polarization beating (the laser excitation) and the entrance to the magnetic field gradient; thus this parameter needs to be optimized experientially. In Fig. 6(a), the nuclear-spin polarization is maximized for an optimal delay $t_B = 10\,\mu s$; simulations for delay times $t_B + / - 1$ μs are also given for comparison. Figure 6(b) shows the evolution of the nuclear polarization as a function of time in the presence of a spatially varying magnetic field, as in Fig. 6(a), but this time for the D_2 molecule. In this example the optimal delay t_B is ~7.5 μs.

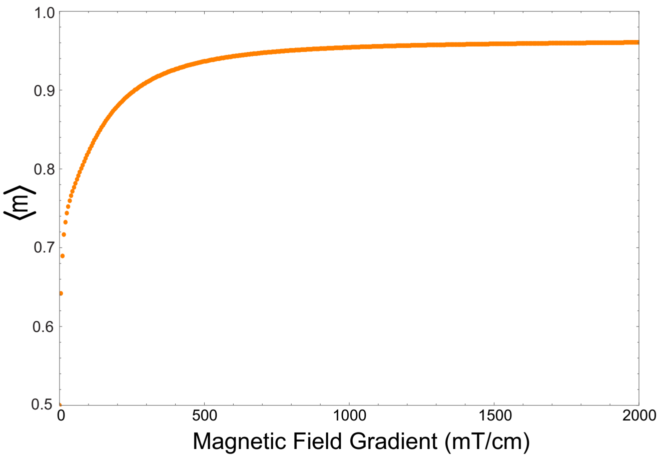

FIG. 7. Example of the maximum nuclear-spin polarization that can be stored, as a function of the magnetic field gradient, for the case of H_2 molecules.

More importantly, the final polarization achieved for H_2 and D_2 molecules when the delay time is varied by 1 μs relative to t_B is shown with the gray lines in both parts (a) and (b) of Fig. 6.

We see that the final polarization value for hydrogen nuclei is much more sensitive to the timing (i.e., position) of the magnetic field than in the deuterium case due to the different frequencies of the hyperfine beatings of the two molecules. In particular, for the $^1\Sigma$ state of H_2 and D_2 molecules, it is the fourth term in Eq. (8) that causes the faster, albeit lower amplitude oscillation, with the amplitude depending on the hyperfine constant d. Timing or positioning the magnetic field gradient to a maximum of this faster oscillation is critical for the final polarization, and since in H_2 the hyperfine constant d is more than twice that for D_2 (see Table I), the fast polarization oscillation, and consequently, the sensitivity to the timing of the magnetic field, is approximatively double.

In Fig. 7 we show the maximum polarization that can be stored, as a function of the magnetic field gradient (of constant slope), for the case of H_2 molecules. As we see, after an initial sharp increase in the area of 0–20 mT/cm, the increase of maximum polarization becomes linear, with a slope of ~1% per 10 mT/cm until 200 mT/cm. For magnetic field gradients larger than 500 mT/cm the polarization increases very slowly; it is practically constant in the area of 700–2000 mT/cm.

IV. CONCLUSION

We have presented studies of polarization dynamics of H_2, HD, and D_2 molecules in the presence of magnetic fields. The hyperfine interaction transfers polarization from nuclear spin to molecular rotation, where it is vulnerable to depolarizing collisions. However, the nuclear spin and the molecular rotation can be decoupled using magnetic fields, and this polarization transfer can be avoided. The calculation presented here can be used in order to determine which magnetic fields are sufficient to prevent depolarization for a given timescale and molecular system.

A useful application of the above is storing hyperpolarized molecules in the presence of magnetic fields. In our examples, molecules are initially prepared in an oriented distribution of their rotational angular momentum. Then the system evolves freely until the polarization transfer to the nuclei is maximized. Finally, the system enters gradually the area of the magnetic field used to preserve hyperpolarization. We show how the modified polarization dynamics can be used to specifically tailor the magnetic field and to design an experiment where hyperpolarization is created and maintained in an optimal way.

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