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Time-dependent polarization transfer from molecular rotation to nuclear spin

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It has been proposed recently that hyperfine depolarization of selected molecular rotational states can be used to produce molecules with highly polarized nuclear spins, and formulas for two distinct nuclei have been given in the limit of hierarchical approximation. Here we present the general, nonhierarchical coupling formalism for the derivation of the $H_{[i]}^{(k)}(I,t)$ factors that govern the time dependence of the nuclear polarizations. The described technique, especially when combined with methods that polarize the electronic angular momentum, can lead to the production of highly polarized atoms from molecular photodissociation, at densities close to that of the parent molecule. In addition, we calculate the time dependence of the H and F nuclear spin polarizations, following the pulsed-laser preparation of the HF $(v=1,J=1,m=1)$ state. It is shown that the polarization of the F and H nuclear spins attain values of about 85% and 70% at time delays of about 1 μs and 4 μs, respectively. Similar results are shown for the pulsed preparation of the DF $(v=0,J=1,m=1)$ state, demonstrating the D atoms can also be significantly polarized.

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I. INTRODUCTION

In recent decades, control over spin and, more generally, over quantum angular momentum has led to many technological advances, such as NMR and medical imaging [1,2], and has allowed the study of many spin-dependent phenomena, such as nuclear, atomic, molecular, and surface scattering [3–5]. Angular momentum polarization also plays a very important role in chemical dynamics, as the spatial direction of the angular momentum of the different species involved in a chemical reaction plays a fundamental role in the way the interaction takes place [6,7].

Methods for producing spin-polarized atoms include Stern-Gerlach separation [8,9], optical pumping [10], and spin-exchange optical pumping [11]. In addition, van Brunt and Zare proposed a method to produce high-density polarized atoms from molecular photodissociation [12], which exploits the fact that the projection of electronic angular momentum in the parent molecule is conserved in the projections of the angular momenta of the atomic photofragments, in the case of prompt photodissociation.

The hyperfine interaction couples the rotational angular momentum **J** and the nuclear spin **I** of a molecule to give the total angular momentum **F**. Pulsed-laser excitation of a particular rotational $|JM\rangle$ state of a molecule often occurs without hyperfine resolution, so that the hyperfine states associated with the particular rotational state are excited coherently. The beating that naturally results in such a situation has been studied theoretically [13] and experimentally [14–17], and is referred to as hyperfine depolarization, which can be viewed, classically, as the precession of **J** and **I** about **F**, and results in the time-dependent transfer of polarization between **J** and **I**. As shown in these studies, the effect of hyperfine depolarization is significant when the molecules are excited in states of relatively low J (when J is approximately equal to I), while it becomes less important when excitation of higher J states is considered (when J is significantly larger than I).

A variety of experiments have been performed where the effects of rotational polarization (either in the reactants or the products) on various aspects of reactivity have been studied. In some of these studies, the effects of hyperfine depolarization need to be taken into account to correct the results for the reduction of the reactant or product polarization [18–29].

Although hyperfine depolarization has been considered traditionally to be a drawback for the production of polarized molecules, the hyperfine coupling of **J** and **I** has recently been proposed as a promising method to produce highly polarized nuclei in molecules [30]. The rotation of isolated molecules is first oriented via pulsed-laser excitation with circularly polarized light (with coherent excitation of the hyperfine components), whereas the nuclear spins are initially unpolarized. The hyperfine beating transfers polarization from **J** to **I**. Prompt photodissociation of the molecules using a laser pulse, carefully timed to coincide with a maximum in the nuclear polarization, allows this polarization to be "frozen in", producing highly polarized atomic nuclei. This, in addition to the highly polarized electronic angular momentum that can arise from the photodissociation process itself [31], allows the production of highly polarized atoms at densities close to the parent molecular density.

The time dependence of the nuclear spin polarization of rotational state-selected molecules, with two nuclear spins, have been reported recently, in the limit of the hierarchical coupling approximation [30]. This approximation is applicable when the coupling of the two nuclear spins to the rotational angular momentum J is significantly different, so that the polarization transfer from the molecule to one nucleus occurs in much shorter time scales than the other. In this paper we present the complete quantum-mechanical treatment in the general case, when the hierarchical coupling approximation does not apply.

In Sec. II we outline the derivation of the nonhierarchical formulas for the hyperfine polarization factors. The proce-

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dure is similar to the derivation of the hyperfine depolarization factor $G^{(k)}(J,t)$ by Altkorn *et al.* [13]; thus, we will emphasize the few differences that exist in the derivation of the nuclear polarization formulas, while all the necessary intermediate steps are shown in the Appendix. In Sec. III we apply these formulas to the well-studied case of HF and discuss the implications of this work to HF and other systems.

II. THEORY

An atomic or molecular gas is polarized when the angular momentum distribution is not isotropic, i.e., the m-state populations, of a particular state J with respect to some laboratory axis, are not all equal. An angular momentum distribution may be described by the $(2J+1)^2$ density matrix elements $\rho_{m'm}$, or equivalently, by the $(2J+1)^2$ multipole moments $A_q^{(k)}(J)$, where k, which is limited to the integer values $0 \leq k \leq 2J$, is the order of the multipole moment. These two sets of parameters are related by the expressions [18,22]

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

and

$$A_q^{(k)}(J) = \frac{c(k)}{\langle Jm|\mathbf{J}^2|Jm\rangle^{k/2}} \sum_{m,m'} \rho_{m'm}\langle Jm|J_q^{(k)}|Jm'\rangle, \tag{1b}$$

where $\langle J\|J^{(k)}\|J\rangle$ are the reduced matrix elements of the rotational angular momentum $\mathbf{J}$, and represents $J_q^{(k)}$ the spherical tensor operators of $\mathbf{J}$ (for a short introduction to the formalism, see Application 13 of [22]), and $c(k)$ are proportionality constants [18].

Although the set of the $\rho_{m'm}$ density matrix elements and the $A_q^{(k)}(J)$ parameters are equivalent, the symmetry of the $A_q^{(k)}(J)$ parameters is more convenient for many applications, in particular those that involve optical excitation, for which the $A_q^{(k)}(J)$ parameters are a much more convenient basis (the constraints of many selection rules are usually expressed much more succinctly). For example, the time dependence of a molecule's polarization, which has been polarized following prompt preparation such as pulsed-laser excitation or as a product of a chemical reaction or photodissociation, is characterized by a time-dependent polarization factor $G^{(k)}(J,t)$ [13],

$$A_q^{(k)}(J,t) = G^{(k)}(J,t)A_q^{(k)}(J,t=0), \tag{2}$$

where

$$G^{(k)}(J,t) = \frac{\langle J^{(k)}(t)\rangle}{\langle J^{(k)}(0)\rangle} = \frac{\langle F_iF\|T^{(k)}(t)\|F_i'F'\rangle}{\langle F_iF\|T^{(k)}(0)\|F_i'F'\rangle} = \frac{\langle J\|J^{(k)}(t)\|J\rangle}{\langle J\|J^{(k)}(0)\|J\rangle}$$

and

$$T^{(k)}(t) = I_2^{(0)}I_1^{(0)}J^{(k)}(t), \tag{3}$$

which has been derived with the use of the Wigner-Eckart theorem [22]. Equation (2) shows that the value of the $A_q^{(k)}(J,t)$ parameter is simply proportional to the initial value of the parameter $A_q^{(k)}(J,t{=}0)$, modified by the factor $G^{(k)}(J,t)$, and there is no mixing of parameters of different rank.

The explicit form of the reduced matrix elements of the $J_q^{(k)}$ tensor is obtained through the evaluation of the reduced matrix elements of a tensor $T^{(k)}$, which is a spherical tensor of rank k constructed from the angular momentum tensor operators in J, I_1, I_2 space [22]. This tensor describes the total angular momentum of the system $T^{(k)}(t){=}I_2^{(0)}I_1^{(0)}J^{(k)}(t)$, in the $|I_2(I_1J)F_iF\rangle$ coupled basis, which yields the expression for $G^{(k)}(J,t)$ [13],

$$G^{(k)}(\mathrm{J},t) = \sum_{\substack{\mathrm{F},\mathrm{F}'\\ \alpha,\alpha'}} \frac{(2\mathrm{F}+1)(2\mathrm{F}'+1)}{(2\mathrm{I}_1+1)(2\mathrm{I}_2+1)} \cos\left[\frac{(\mathrm{E}_{\alpha,\mathrm{F}}-\mathrm{E}_{\alpha',\mathrm{F}'})t}{\hbar}\right] \times \left(\sum_{\mathrm{F}_i,\mathrm{F}_i'}(-1)^{\mathrm{F}_i+\mathrm{F}_i'}\sqrt{(2\mathrm{F}_i+1)(2\mathrm{F}_i'+1)} \times \begin{Bmatrix} \mathrm{F}_i' & \mathrm{J} & \mathrm{I}_1 \\ \mathrm{J} & \mathrm{F}_i & \mathrm{k} \end{Bmatrix} \begin{Bmatrix} \mathrm{F}_i' & \mathrm{F}' & \mathrm{I}_2 \\ \mathrm{F} & \mathrm{F}_i & \mathrm{k} \end{Bmatrix} \mathrm{C}^{(\mathrm{F})}_{\mathrm{F}_i,\alpha}\mathrm{C}^{(\mathrm{F}')*}_{\mathrm{F}_i',\alpha'}\right)^2, \tag{4}$$

where F is the quantum number associated with the total angular momentum $\mathbf{F}{=}\mathbf{J}{+}\mathbf{I}_1{+}\mathbf{I}_2$. F_i represents an intermediate coupling quantum number associated with $\mathbf{F}_i{=}\mathbf{I}_1{+}\mathbf{J}$, which is a good quantum number in the limit of hierarchical coupling. In such a case the hyperfine energy levels are calculated in the $|F,F_i\rangle$ basis. The energies that correspond to the general, nonhierarchical coupling are obtained by diagonalizing the hyperfine Hamiltonian in this basis. Thus, they depend not on F_i but on α, a quantum number that represents a less specific coupling, the one that diagonalizes the hyperfine Hamiltonian. Assigning particular values to α is not necessary for the evaluation of (4), since these indices serve only to distinguish the eigenenergies and to connect them to the appropriate eigenvector elements labeled here as $C^F_{F_i,\alpha}$. This notation was established by Altkorn *et al.* [13] in their derivation of the expression (4), for the rotational depolarization factor. This notation is followed here as well, in our similar derivation of the $H_{[i]}^{(k)}(I,t)$ polarization factors.

The time dependence of the polarization of each nucleus is similarly governed by a time-dependent polarization factor, $H_{[i]}^{(k)}(I,t)$, which relates the spatial distribution of the nuclear spin, I, with the original molecular polarization of J,

$$A_q^{(k)}(I,t) = H_{[i]}^{(k)}(I,t)A_q^{(k)}(J,t=0) \tag{5}$$

Leaving the evaluation of the reduced matrix elements to be discussed in the Appendix, we present here the final expression for the polarization factors for I_1 and I_2, respectively:

$$H^{(k)}_{[1]}(I_1,t)=\frac{U_k(I_1)}{U_k(J)}\sum_{F,F'}\frac{(2F+1)(2F'+1)}{(2I_2+1)\sqrt{(2I_1+1)(2J+1)}}\sum_{\alpha\alpha'}\cos\left[\frac{(E_{\alpha,F}-E_{\alpha',F'})t}{\hbar}\right]$$
$$\times\sum_{F_i,F_i'}(-1)^{2F_i'}\sqrt{(2F_i+1)(2F_i'+1)}C^{(F)}_{F_i,\alpha}C^{(F')*}_{F_i',\alpha'}\begin{Bmatrix}F_i & F_i' & k\\ F' & F & I_2\end{Bmatrix}\begin{Bmatrix}F_i & F_i' & k\\ I_1 & I_1 & J\end{Bmatrix}$$
$$\times\sum_{F_i'',F_i'''}(-1)^{F_i''+F_i'''}\sqrt{(2F_i''+1)(2F_i'''+1)}C^{(F')}_{F_i''',\alpha}C^{(F)*}_{F_i'',\alpha'}\begin{Bmatrix}F_i'' & F_i''' & k\\ F' & F & I_2\end{Bmatrix}\begin{Bmatrix}F_i'' & F_i''' & k\\ J & J & I_1\end{Bmatrix},\qquad(6)$$

and

$$H^{(k)}_{[2]}(I_2,t)=\frac{U_k(I_2)}{U_k(J)}\sum_{F,F'}\frac{(2F+1)(2F'+1)}{(2I_1+1)\sqrt{(2I_2+1)(2J+1)}}\sum_{\alpha\alpha'}(-1)^{I_1+J+k+F'}\cos\left[\frac{(E_{\alpha,F}-E_{\alpha',F'})t}{\hbar}\right]$$
$$\times\sum_{F_i,F_i'}(-1)^{F_i+F_i'}\sqrt{(2F_i+1)(2F_i'+1)}C^{(F)}_{F_i,\alpha}C^{(F')*}_{F_i',\alpha'}\begin{Bmatrix}F_i & F_i' & k\\ F' & F & I_2\end{Bmatrix}\begin{Bmatrix}F_i & F_i' & k\\ J & J & I_1\end{Bmatrix}\sum_{F_i''}(-1)^{3F_i''-F}C^{(F')}_{F_i'',\alpha}C^{(F)*}_{F_i'',\alpha'}\begin{Bmatrix}F' & F & k\\ I_2 & I_2 & F_i''\end{Bmatrix}.\qquad(7)$$

The subscript $[i]$ refers to the order in which the nuclei have been coupled. For example, $H^{(k)}_{[1]}(I_1,t)$ refers to the time dependence of the polarization of nucleus I_1, for which we have first coupled J and I_1 followed by I_2, whereas $H^{(k)}_{[2]}(I_1,t)$ refers also to the polarization of I_1, but for which we have first coupled J and I_2 followed by I_1. Of course, $H^{(k)}_{[1]}(I_1,t)$ and $H^{(k)}_{[2]}(I_1,t)$ must be equal, which is not immediately obvious by comparing Eqs. (6) and (7). The $U_k(J)$ are equal to the reciprocals of the $V_k(J)$ and $f^k(J)$ defined in [32] and [33], respectively. They are normalization constants that rescale the $A^{(k)}_q(J,t)$ to the $A^{(k)}_q(I,t)$ for different values of I and J, and take the values $U(J)=1$, and $U_2(J)=\{(2J-1)(2J+3)/[J(J+1)]\}^{1/2}$.

Conservation of the projection of angular momentum,

$$\langle m_J(t)\rangle+\langle m_{I_1}(t)\rangle+\langle m_{I_2}(t)\rangle=\langle m_J(0)\rangle,\qquad(8)$$

can be expressed as

$$G^{(1)}(t)+\sqrt{\frac{I_1(I_1+1)}{J(J+1)}}H^{(1)}_{[1]}(I_1,t)+\sqrt{\frac{I_2(I_2+1)}{J(J+1)}}H^{(1)}_{[2]}(I_2,t)=1,\qquad(9)$$

using $\langle m_J(t)\rangle$ equal to $\sqrt{J(J+1)}A^{(1)}_0(J,t)$ [33], using similar expressions for the other projections, and Eqs. (2) and (5). Equation (9) is a useful check of the correct use of Eqs. (4), (6), and (7), and we use this check in the calculations plotted below.

When the hierarchical approximation is applied, F_i is considered to be a good quantum number which coincides with α, and thus $C^{(F)}_{F_i,\alpha}=\delta_{F_i,\alpha}$. In this situation, the nuclear polarization expressions $H^{(k)}_{[1]}(I_1,t)$ and $H^{(k)}_{[2]}(I_2,t)$ can be simplified to (see Appendix)

$$H^{(k)}_{[1]}(I_1,t)=\frac{U_k(I_1)}{U_k(J)}\sum_{\substack{F,F'\\F_i,F_i'}}(-1)^{F_i'-F_i}$$
$$\times\frac{(2F+1)(2F'+1)(2F_i+1)(2F_i'+1)}{(2I_2+1)\sqrt{(2I_1+1)(2J+1)}}$$
$$\times\cos\left[\frac{(E_{F_i,F}-E_{F_i',F'})t}{\hbar}\right]\begin{Bmatrix}F_i & F_i' & k\\ I_1 & I_1 & J\end{Bmatrix}$$
$$\times\begin{Bmatrix}F_i & F_i' & k\\ J & J & I_1\end{Bmatrix}\begin{Bmatrix}F_i & F_i' & k\\ F' & F & I_2\end{Bmatrix}^2\qquad(10)$$

and

$$H^{(k)}_{[2]}(I_2,t)=\frac{U_k(I_2)}{U_k(J)}\sum_{F,F'}\sum_{F_i}(-1)^{(I_1+J+k+F'-F+F_i)}$$
$$\times\frac{(2F+1)(2F'+1)(2F_i+1)}{(2I_1+1)\sqrt{(2I_2+1)(2J+1)}}$$
$$\times\cos\left[\frac{(E_{F_i,F}-E_{F_i,F'})t}{\hbar}\right]\begin{Bmatrix}F' & F & k\\ I_2 & I_2 & F_i\end{Bmatrix}$$
$$\times\begin{Bmatrix}F' & F & k\\ F_i & F_i & I_2\end{Bmatrix}\begin{Bmatrix}F_i & F_i & k\\ J & J & I_1\end{Bmatrix},\qquad(11)$$

while (4) reduces to

$$G^{(k)}(J,t)=\sum_{F,F'}\sum_{F_i,F_i'}\frac{(2F+1)(2F'+1)(2F_i+1)(2F_i'+1)}{(2I_1+1)(2I_2+1)}\times\begin{Bmatrix} F_i' & J & I_1\\ J & F_i & k\end{Bmatrix}^2\begin{Bmatrix} F_i' & F' & I_2\\ F & F_i & k\end{Bmatrix}^2\times\cos\left[\frac{(E_{F_i,F}-E_{F_i',F'})t}{\hbar}\right]. \qquad (12)$$

In the simplest case where the molecule possesses one or more indistinguishable nuclei, or only one of the nuclei has nonzero spin (i.e., $I_2=0$ and $I_1=I$), Eq. (12) is simplified and the molecular depolarization is described by

$$G^{(k)}(J,t)=\sum_{F,F'}\frac{(2F+1)(2F'+1)}{(2I+1)}\begin{Bmatrix} F' & F & k\\ J & J & I\end{Bmatrix}^2\times\cos\left[\frac{(E_F-E_{F'})t}{\hbar}\right], \qquad (13)$$

whereas Eq. (10) is also simplified, and the nuclear polarization of I is described by

$$H^{(k)}(I,t)=\frac{U_k(I)}{U_k(J)}\sum_{F,F'}(-1)^{F-F'}\times\frac{(2F+1)(2F'+1)}{\sqrt{(2I+1)(2J+1)}}\cos\left[\frac{(E_F-E_{F'})t}{\hbar}\right]\times\begin{Bmatrix} F' & F & k\\ J & J & I\end{Bmatrix}\begin{Bmatrix} F' & F & k\\ I & I & J\end{Bmatrix}. \qquad (14)$$

III. DISCUSSION

In this section we examine the well-studied system of HF and plot the time dependence of the polarization of J and the H and F nuclear spins (i.e., the $G^{(k)}(J,t)$ and $H^{(k)}_{[i]}(I,t)$ factors) following the prompt preparation of the HF ($v=1,J=1,m=1$) state. The computer program that has been used to evaluate the relevant formulas uses the information available from high-resolution spectroscopic measurements. In particular, the hyperfine Hamiltonian used, in the absence of electromagnetic fields, is [34]

$$H=C_F(\mathbf{I}_F\cdot\mathbf{J})+C_H(\mathbf{I}_H\cdot\mathbf{J})+J_{HF}(\mathbf{I}_H\cdot\mathbf{I}_F)+[S_{HF}/(2J+3)(2J-1)][3(\mathbf{I}_H\cdot\mathbf{J})(\mathbf{I}_F\cdot\mathbf{J})+3(\mathbf{I}_F\cdot\mathbf{J})(\mathbf{I}_H\cdot\mathbf{J})-2(\mathbf{I}_H\cdot\mathbf{I}_F)J(J+1)], \qquad (15)$$

where the values for the hyperfine structure constants are $C_F=307.637$ kHz, $C_H=-71.128$ kHz, $S_{HF}=28.675$ kHz, and $J_{HF}=0.529$ kHz, for the lowest vibrational state $v=0$ and the first excited rotational state $J=1$ [34]. The corresponding values for higher vibrational and rotational states are calculated as

$$C_{H,F}(v,J)=C_{H,F}(v=0,J=0)+a_{H,F}v+b_{H,F}J(J+1), \qquad (16)$$

with $a_F=53$ kHz, $a_H=1.99$ kHz, $b_F=0.17$ kHz, and $b_H=0.036$ kHz [35]. Figure 1 shows the time dependence of the $G^{(2)}(J,t)$ factors, which describe the depolarization of the alignment of the HF ($v=1,J=1,m=1$) state. As we see, significant disagreement between the hierarchical [Eq. (4)] and nonhierarchical expression [Eq. (12)] appears only in very large times, where the hierarchical approximation's solution appears somewhat slower. This is a natural consequence of the hierarchical approximation, which implies that all the polarization exchange occurs through $\mathbf{F_i}=\mathbf{J}+\mathbf{I_1}$, which for HF is the dominant coupling, but not the only one. Of course, the differences shown here occur on time scales not interesting for most experimental purposes; nevertheless, it is useful to see how the two approaches perform in a real system.

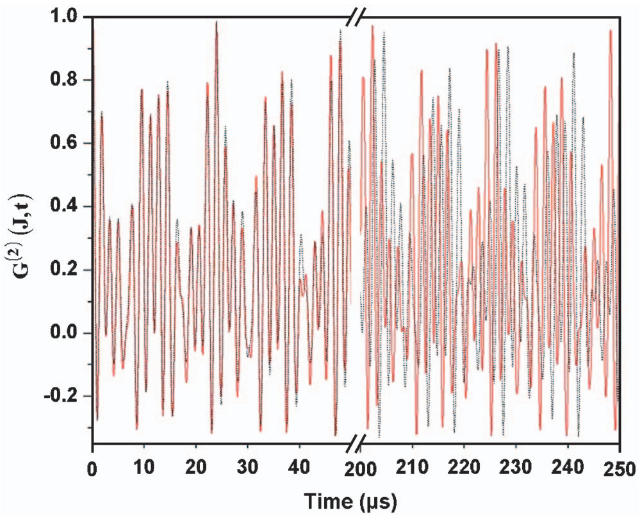

FIG. 1. (Color online) The molecular depolarization factor $G^{(2)}(J,t)$ that determines the time dependence of the rotational alignment, as calculated from the general nonhierarchical expression of Eq. (2) (solid red line), and from the hierarchical approximation of Eq. (8) (dashed black line).

In Fig. 2 we see the evolution of $G^{(1)}(J,t)$ that governs rotational orientation and the corresponding nuclear spin orientation, calculated with the general, nonhierarchical formulas (4), (6), and (7). The products $\sqrt{[I_1(I_1+1)/J(J+1)]}H^{(k)}_{[1]}(I_1,t)$, and $\sqrt{[I_2(I_2+1)/J(J+1)]}\times H^{(k)}_{[2]}(I_2,t)$ directly correspond to $\langle m_1\rangle$ and $\langle m_2\rangle$, respectively. As we see in Fig. 2, these products vary in a complementary fashion with respect to $G^{(1)}(t)$, so that they satisfy conservation of the projection of angular momentum as expressed in (9).

Figure 2 shows that the values of $H^{(1)}(I_1,t)$ and $H^{(1)}(I_2,t)$ almost reach their maximum values at about 1 and 4 μs. This temporal behavior can be explained by the different values of the hyperfine constants that couple each nuclear spin to the molecular rotation. In the HF molecule in particular, the ratio of these constants is $C_F/C_H\sim 5.3$ (for $v=J=1$) [34], and this situation has an approximate correspondence to the relative frequencies of the nuclear polarization beatings. It should be noted here that if the time-averaged polarization of the nuclear spins is detected, instead of the maximum nuclear polarizations that can be obtained at specific times, the polarization obtained is going to be much smaller. For the

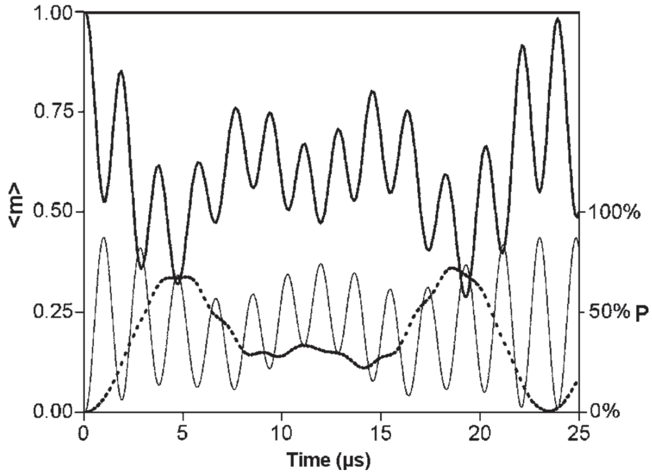

FIG. 2. The time dependence of $\langle m_{J_{HF}}\rangle$ (bold line), $\langle m_{I_F}\rangle$ (solid line), and $\langle m_{I_H}\rangle$ (dotted line) as well as their summation (which is always 1) for the prompt preparation of the HF $(v=1,J=1,m=1)$ rovibrational state without hyperfine resolution. Note that all three plots always sum to unity (the initial projection of m_J).

situation presented in Fig. 2, the average molecular depolarization and corresponding nuclear polarization will be $\langle m_J\rangle=0.596$, $\langle m_{I_F}\rangle=0.213$, and $\langle m_{I_H}\rangle=0.191$. The average depolarization and polarization values satisfy conservation of angular momentum as expressed in (9). Application of the hierarchical approximation expressed in Eqs. (10)–(12) give slightly smoother plots for the polarization factor, and as shown in Fig. 1 fail only at very large times.

We consider now the case of the pulsed excitation of the $(v=0,J=1,m=1)$ state of DF, for which the hierarchical approximation can no longer be used to reasonable approximation. We use the same Hamiltonian as in Eq. (15), except by replacing I_H, C_H, and S_{HF} by I_D, C_D, and S_{DF}, and adding the following term for the interaction of the quadrupole moment of $\mathbf{I}_D$ with $\mathbf{J}$,

$$H_Q=-\left[\frac{(eqQ)_D}{2I_D(2I_D-1)(2J-1)(2J+3)}\right]\times\left[3(\mathbf{I}_D\cdot\mathbf{J})^2+\frac{3}{2}(\mathbf{I}_D\cdot\mathbf{J})-(\mathbf{I}_D^2\mathbf{J}^2)\right]. \tag{17}$$

The hyperfine energies are calculated by using the constants $C_F=158.356$ kHz, $C_D=-5.755$ kHz, $S_{DF}=4.434$ kHz, $J_{DF}=0$ (no experimental measurement is given), and $(eqQ)_D=354.238$ kHz [34], and $I_D=1$. In Fig. 3 we show the time evolution of the polarization of $\mathbf{J}$, $\mathbf{I}_D$, and $\mathbf{I}_F$ following pulsed excitation of the $(v=0,J=1,m=1)$ state of DF, for the case of (a) nonhierarchical coupling, using Eq. (4), (6), and (7), and (b) the case of hierarchical coupling, using Eq. (10)–(12). We see that even though the same hyperfine energies have been used in both cases, the time evolution is significantly different for the two cases, and we therefore show that the complete nonhierarchical formalism is necessary to describe a system such as DF. We also note that D nuclei with $\langle m_D\rangle\approx 0.6$ can be produced by exciting the $(v=0,J=1,m=1)$ state of DF, and by photodissociating after about 4.5 μs.

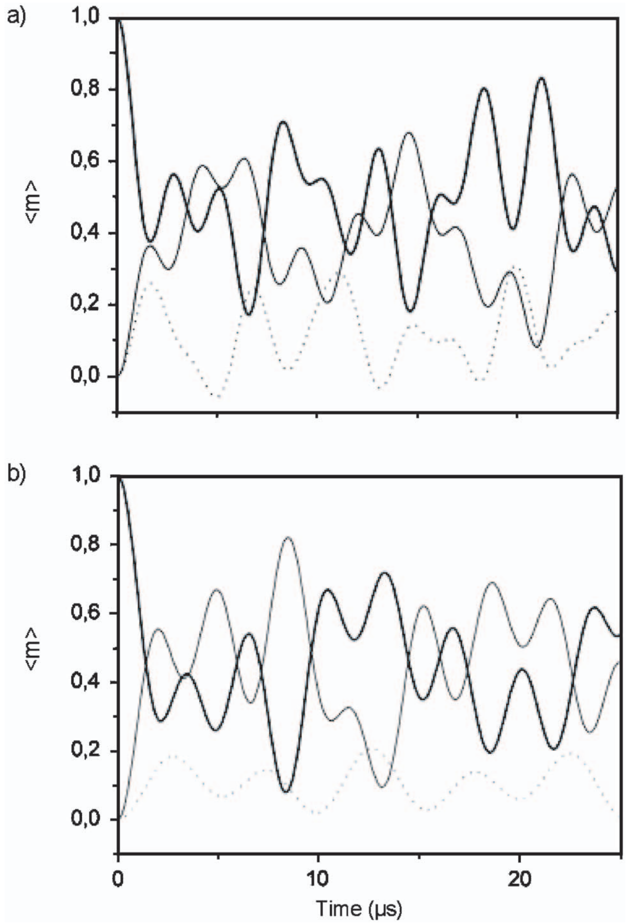

FIG. 3. The time dependence of $\langle m_{J_{DF}}\rangle$ (bold line), $\langle m_{I_D}\rangle$ (solid line), and $\langle m_{I_F}\rangle$ (dotted line) as well as their summation (which is always 1) for the prompt preparation of the DF $(v=0,J=1,m=1)$ rovibrational state without hyperfine resolution, for calculations using (a) the nonhierarchical coupling expressions of Eqs. (4), (6), and (7), and (b) the hierarchical coupling expressions of Eqs. (10)–(12). Note that all three plots always sum to unity.

The formalism presented here, except for proofs of the hierarchical formulas of [30], allows the description of a larger variety of molecular systems. The simplest possible situation is when the molecule possesses one nonzero nuclear spin or possesses two or more indistinguishable nuclei. In such cases, for example OH, H_2, or CH_4, formulas (13) and (14) apply. The approximate hierarchical formulas apply in the case where the coupling of one nuclear spin is much stronger than the other. All of the hydrogen halides except HF exhibit strong quadrupole coupling for the halogen nuclei so that the polarization dependence is very well described by the hierarchical expressions of Eq. (10)–(12). Even in the case of HF, where $I_F=1/2$ and does not possess a quadrupole moment, we find that the hierarchical approximation is still quite accurate. On the other hand, the general, nonapproximating formalism will be necessary for molecules for which the coupling strengths of the two nuclei are similar such as DF, and for molecules consisting of two isotopes of the same nuclei such as $^{35}Cl^{37}Cl$, HD, HT, etc. Those, and more examples, interesting for their potential use as a source for polarized atoms are currently under study, and we hope to present their properties in future work.

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APPENDIX

The time dependence of the first nuclei’s polarization is characterized by a time-dependent polarization factor

$$H_{[1]}^{(k)}(I_1,t)=\left(\frac{J(J+1)}{I_1(I_1+1)}\right)^{k/2}\frac{\langle I_1^{(k)}(t)\rangle}{\langle J^{(k)}(0)\rangle}=\left(\frac{J(J+1)}{I_1(I_1+1)}\right)^{k/2}\frac{\langle F_iF\|X^{(k)}(t)\|F_i'F'\rangle}{\langle F_iF\|T^{(k)}(0)\|F_i'F'\rangle},\tag{A1}$$

where $X^{(k)}(t)=I_2^{(0)}I_1^{(k)}(t)J^{(0)}$ and $X^{(k)}(t)=e^{iHt/\hbar}X^{(k)}(0)e^{-(iHt/\hbar)}$. Following Alkorn’s notation, we will refer to S(14.66) and FR(15.15) as the 14.66 and 15.15 expressions of Refs. [36,37], respectively. Applying FR(15.15) leads to

$$\langle F_iF\|I_2^{(0)}I_1^{(k)}(t)J^{(0)}\|F_i'F'\rangle=\sum_{F_i'',F_i'''}\frac{\langle F_iF\|e^{iHt/\hbar}\|F_i''F\rangle}{(2F+1)^{1/2}}\langle F_i''F\|I_2^{(0)}I_1^{(k)}(t)J^{(0)}\|F_i'''F'\rangle\frac{\langle F_i'''F'\|e^{-(iHt/\hbar)}\|F_i'F'\rangle}{(2F'+1)^{1/2}},\tag{A2}$$

while application of S(14.66) leads to

$$\begin{aligned}\langle F_iF\|I_2^{(0)}I_1^{(k)}(t)J^{(0)}\|F_i'F'\rangle&=\langle I_2\|I_2^{(0)}\|I_2\rangle\langle I_1\|I_1^{(k)}\|I_1\rangle\langle J\|J^{(0)}\|J\rangle\sum_{F_i'',F_i'''}\sqrt{(2F+1)(2F'+1)(2F_i''+1)(2F_i'''+1)}(2k+1)\\&\quad\times\frac{\langle F_iF\|e^{iHt/\hbar}\|F_i''F\rangle}{(2F+1)^{1/2}}\begin{Bmatrix}I_1&I_1&k\\J&J&0\\F_i''&F_i'''&k\end{Bmatrix}\begin{Bmatrix}I_2&I_2&0\\F_i''&F_i'''&k\\F&F'&k\end{Bmatrix}\frac{\langle F_i'''F'\|e^{-(iHt/\hbar)}\|F_i'F'\rangle}{(2F'+1)^{1/2}}.\end{aligned}\tag{A3}$$

The reduced matrix element $\langle F_iF\|T^{(k)}(0)\|F_i'F'\rangle$ can be evaluated by application of S(14.66),

$$\langle F_iF\|I_2^{(0)}I_1^{(0)}J^{(k)}\|F_i'F'\rangle=\sqrt{(2F+1)(2F'+1)(2F_i'+1)(2F_i+1)}(2k+1)\langle I_2\|I_2^{(0)}\|I_2\rangle\langle I_1\|I_1^{(0)}\|I_1\rangle\langle J\|J^{(\mathrm{k})}(0)\|J\rangle\begin{Bmatrix}I_1&I_1&0\\J&J&k\\F_i&F_i'&k\end{Bmatrix}\begin{Bmatrix}I_2&I_2&0\\F_i&F_i'&k\\F&F'&k\end{Bmatrix}.\tag{A4}$$

Thus, the ratio of the reduced matrix elements in (A1) equals

$$\begin{aligned}\frac{\langle F_iF\|I_2^{(0)}I_1^{(k)}(t)J^{(0)}\|F_i'F'\rangle}{\langle F_iF\|I_2^{(0)}I_1^{(0)}J^{(k)}(0)\|F_i'F'\rangle}&=\frac{\langle I_1\|I_1^{(k)}\|I_1\rangle\langle J\|J^{(0)}\|J\rangle}{\langle J\|J^{(k)}(0)\|J\rangle\langle I_1\|I_1^{(0)}\|I_1\rangle}\sum_{F_i'',F_i'''}\sqrt{(2F+1)(2F'+1)(2F_i''+1)(2F_i'''+1)}(2k+1)\\&\quad\times\frac{\displaystyle\sum_{\alpha,\alpha}C_{F_i\alpha}^{(F)}C_{F_i''\alpha'}^{(F)*}C_{F_i'''\alpha}^{(F')}C_{F_i'\alpha'}^{(F')*}\cos\left[\frac{E_{\alpha,F}-E_{\alpha',F'}}{\hbar}t\right]\begin{Bmatrix}I_1&I_1&k\\J&J&0\\F_i''&F_i'''&k\end{Bmatrix}\begin{Bmatrix}I_2&I_2&0\\F_i''&F_i'''&k\\F&F'&k\end{Bmatrix}}{\sqrt{(2F+1)(2F'+1)(2F_i+1)(2F_i'+1)}(2k+1)\begin{Bmatrix}I_1&I_1&0\\J&J&k\\F_i&F_i'&k\end{Bmatrix}\begin{Bmatrix}I_2&I_2&0\\F_i&F_i'&k\\F&F'&k\end{Bmatrix}}.\end{aligned}\tag{A5}$$

We multiply both the numerator and the denominator of this ratio with

$$\begin{Bmatrix}I_1&I_1&0\\J&J&k\\F_i&F_i'&k\end{Bmatrix}\begin{Bmatrix}I_2&I_2&0\\F_i&F_i'&k\\F&F'&k\end{Bmatrix}\sqrt{(2F+1)(2F'+1)(2F_i+1)(2F_i'+1)}(2k+1),\tag{A6}$$

and we sum over F_i,F,F_i',F' to obtain the orthonormality relation of the 9-j symbols. After rearranging the terms we obtain

$$\frac{\langle F_iF\|I_2^{(0)}I_1^{(k)}(t)J^{(0)}\|F_i'F'\rangle}{\langle F_iF\|I_2^{(0)}I_1^{(0)}J^{(k)}(0)\|F_i'F'\rangle} = \frac{\langle I_1\|I_1^{(k)}\|I_1\rangle\langle J\|J^{(0)}\|J\rangle}{\langle J\|J^{(k)}(0)\|J\rangle\langle I_1\|I_1^{(0)}\|I_1\rangle}\sum_{F,F'}(2F+1)(2F'+1)(2k+1)^2\sum_{\alpha,\alpha'}\cos\left[\frac{E_{\alpha,F}-E_{\alpha',F'}}{\hbar}t\right]$$
$$\times\sum_{F_i,F_i'}C_{F_i,\alpha}^{(F)}C_{F_i',\alpha'}^{(F')*}\sqrt{(2F_i+1)(2F_i'+1)}\begin{Bmatrix} I_1 & I_1 & k\\ J & J & 0\\ F_i & F_i' & k\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & 0\\ F_i & F_i' & k\\ F & F' & k\end{Bmatrix}$$
$$\times\sum_{F_i'',F_i'''}C_{F_i'',\alpha}^{(F)*}C_{F_i''',\alpha'}^{(F')}\sqrt{(2F_i''+1)(2F_i'''+1)}\begin{Bmatrix} I_1 & I_1 & 0\\ J & J & k\\ F_i'' & F_i''' & k\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & 0\\ F_i'' & F_i''' & k\\ F & F' & k\end{Bmatrix}, \tag{A7}$$

and thus,

$$\frac{A_q^k[I_1,t]}{A_q^k[J,0]} = \left(\frac{J(J+1)}{I_1(I_1+1)}\right)^{k/2}\frac{\langle I_1\|I_1^{(k)}\|I_1\rangle\langle J\|J^{(0)}\|J\rangle}{\langle J\|J^{(k)}(0)\|J\rangle\langle I_1\|I_1^{(0)}\|I_1\rangle}\sum_{F,F'}(2F+1)(2F'+1)(2k+1)^2$$
$$\times\sum_{\alpha,\alpha'}\cos\left[\frac{E_{\alpha,F}-E_{\alpha',F'}}{\hbar}t\right]\sum_{F_i,F_i'}C_{F_i,\alpha}^{(F)}C_{F_i',\alpha'}^{(F')*}\sqrt{(2F_i+1)(2F_i'+1)}\begin{Bmatrix} I_1 & I_1 & k\\ J & J & 0\\ F_i & F_i' & k\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & 0\\ F_i & F_i' & k\\ F & F' & k\end{Bmatrix}$$
$$\times\sum_{F_i'',F_i'''}C_{F_i'',\alpha}^{(F)*}C_{F_i''',\alpha'}^{(F')}\sqrt{(2F_i''+1)(2F_i'''+1)}\begin{Bmatrix} I_1 & I_1 & 0\\ J & J & k\\ F_i'' & F_i''' & k\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & 0\\ F_i'' & F_i''' & k\\ F & F' & k\end{Bmatrix}. \tag{A8}$$

Reducing the 9-j symbols to the corresponding 6-j symbols, and using Eq. (5), we obtain Eq. (6), where the leading constants have been collected into the ratio $U_k(I_1)/U_k(J)$. Applying the conditions for hierarchical coupling ($C_{F_i,\alpha}^{(F)}=\delta_{F_i,\alpha}$) gives the hierarchical coupling description, Eq. (10), for $H_{[1]}^{(k)}(I_1,t)$.

In a similar manner, we obtain the following expression for the time dependence of the polarization of nucleus I_2:

$$\frac{A_q^k[I_2,t]}{A_q^k[J,0]} = \left(\frac{J(J+1)}{I_2(I_2+1)}\right)^{k/2}\frac{\langle I_2\|I_2^{(k)}\|I_2\rangle\langle J\|J^{(0)}\|J\rangle}{\langle J\|J^{(k)}(0)\|J\rangle\langle I_2\|I_2^{(0)}\|I_2\rangle}\sum_{F,F'}(2F+1)(2F'+1)(2k+1)^{3/2}$$
$$\times\sum_{\alpha,\alpha'}\cos\left[\frac{E_{\alpha,F}-E_{\alpha',F'}}{\hbar}t\right]\sum_{F_i,F_i'}C_{F_i\alpha}^{(F)}C_{F_i'a'}^{(F')*}\sqrt{(2F_i+1)(2F_i'+1)}\begin{Bmatrix} I_1 & I_1 & 0\\ J & J & 0\\ F_i & F_i' & 0\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & k\\ F_i & F_i' & 0\\ F & F' & k\end{Bmatrix}$$
$$\times\sum_{F_i'',F_i'''}C_{F_i'',\alpha}^{(F)*}C_{F_i''',\alpha'}^{(F')}\sqrt{(2F_i''+1)(2F_i'''+1)}\begin{Bmatrix} I_1 & I_1 & 0\\ J & J & k\\ F_i'' & F_i''' & k\end{Bmatrix}\begin{Bmatrix} I_2 & I_2 & 0\\ F_i'' & F_i''' & k\\ F & F' & k\end{Bmatrix}. \tag{A9}$$

Reducing the 9-j symbols with a vanishing element to 6-j symbols (e.g., using Eq. 4.25 in [22]) gives, in the general case, Eq. (7), whereas applying the conditions for hierarchical coupling ($C_{F_i,\alpha}^{(F)}=\delta_{F_i,\alpha}$) first and then reducing the 9-j symbols gives the hierarchical coupling description of Eq. (11).

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[1] R. J. Abraham, J. Fisher, and P. Loftus, *Introduction to NMR spectroscopy* (Wiley, New York, 1998).

[2] M. S. Albert, G. D. Cates, W. Happer, B. Saam, C. S. Springer, and A. Wishnia, Nature (London) **370**, 199 (1994).

[3] S. G. Redsun, R. J. Knize, G. D. Cates, and W. Happer, Phys. Rev. A **42**, 1293 (1990).

[4] E. Steffens and W. Haeberli, Rep. Prog. Phys. **66**, 1887 (2003).

[5] C. T. Rettner and R. N. Zare, J. Chem. Phys. **77**, 2416 (1982).

[6] P. R. Brooks and E. M. Jones, J. Chem. Phys. **45**, 3449 (1966).

[7] R. N. Zare, Science **279**, 1875 (1978).

[8] W. Gerlach and O. Stern, Ann. Phys Lpz. **74**, 673 (1924).

[9] K. Zapfe *et al.*, Rev. Sci. Instrum. **66**, 28 (1995).

[10] W. Happer, Rev. Mod. Phys. **44**, 169 (1972).

[11] S. Appelt, A.B. Baranga, C. J. Erickson, M. V. Romalis, A. R. Young, and W. Happer, Phys. Rev. A **58**, 1412 (1998).

[12] R. J. van Brunt and R. N. Zare, J. Chem. Phys. **48**, 4304 (1968).

[13] R. Altkorn, R. N. Zare, and C. H. Greene, Mol. Phys. **55**, 1 (1985).
[14] J. Zhang, C. W. Riehn, M. Dulligan, and C. Wittig, J. Chem. Phys. **104**, 7027 (1996).
[15] A. J. Orr-Ewing, W. R. Simpson, T. P. Rakitzis, and R. N. Zare, Isr. J. Chem. **34**, 95 (1994).
[16] M. L. Costen and G. E. Hall, Phys. Chem. Chem. Phys. **7**, 1408 (2005).
[17] H. Lammer, R. T. Carter, and J. R. Huber, Eur. Phys. J. D **8**, 385 (2000).
[18] A. J. Orr-Ewing and R. N. Zare, Annu. Rev. Phys. Chem. **45**, 315 (1994).
[19] F. Green, G. Hancock, A. J. Orr-Ewing, M. Brouard, S. P. Duxon, P. A. Enriquez, R. Sayos, and J. P. Simons, Chem. Phys. Lett. **182**, 568 (1991).
[20] S. A. Kandel, A. J. Alexander, Z. H. Kim, R. N. Zare, F. J. Aoiz, L. Banares, J. F. Castillo, and V. S. Rabanos, J. Chem. Phys. **112**, 670 (2000).
[21] C. H. Greene and R. N. Zare, Annu. Rev. Phys. Chem. **33**, 119 (1982).
[22] R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
[23] A. J. Orr-Ewing, W. R. Simpson, T. P. Rakitzis, S. A. Kandel, and R. N. Zare, Chem. Phys. **106**, 5961 (1997).
[24] M. Rutkowski and H. Zacharias, Chem. Phys. **301**, 189 (2004).
[25] M. L. Costen and K. G. McKendrick, J. Chem. Phys. **122**, 164309-1 (2005).
[26] N. Hemmi and T. A. Cool, J. Chem. Phys. **105**, 7964 (1996).
[27] R. P. Wood, C. H. Greene, and D. Armstrong, Phys. Rev. A **47**, 229 (1993).
[28] A. G. Evseev, Kupriyanov, B. V. Picheyev, B. N. Sevastianov, and O. S. Vasyutinskii, Chem. Phys. **171**, 45 (1993).
[29] E. R. Wouters, L. D. A. Siebbeles, K. L. Reid, B. Buijsse, and W. J. van der Zande, Chem. Phys. **218**, 309 (1997).
[30] T. P. Rakitzis, Phys. Rev. Lett. **94**, 083005 (2005).
[31] T. P. Rakitzis, P. C. Samartzis, R. L. Toomes, T. N. Kitsopoulos, Alex Brown, G. G. Balint-Kurti, O. S. Vasyutinskii, and J. A. Beswick, Science **300**, 1936 (2003).
[32] G. G. Balint-Kurti, A. J. Orr-Ewing, J. A. Beswick, A. Brown, and O. S. Vasyutinskii, J. Chem. Phys. **116**, 10760 (2002).
[33] M. P. Docker, Chem. Phys. **135**, 405 (1989).
[34] J. S. Muenter and W. Klemperer, J. Chem. Phys. **52**, 6033 (1970).
[35] C. Breant, T. Baer, D. Nesbitt, and J. L. Hall, *Sixth International Conference on Laser Spectroscopy* (Springer, New York, 1983), Vol. 138.
[36] I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Pergammon Press, New York, 1972).
[37] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press, New York, 1959).