Invited Article

Depolarization of optically prepared molecules by two randomly oriented spins

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A general expression is developed for the time development of the alignment of an ensemble of isolated molecules having two random internal spins when the ensemble is optically pumped by absorption of a linearly polarized light pulse. This derivation assumes that the internal spin structure (fine structure/hyperfine structure) is coherently excited and is not resolved. As an example the pulsed infrared excitation of hydrogen fluoride is considered, in particular the vibration–rotation transition $HF(v'' = 0, N'') \rightarrow HF(v = 1, N)$. The presence of the nuclear spins $I_H = \frac{1}{2}$ and $I_F = \frac{1}{2}$ is found to cause a significant reduction in the degree of alignment of the low rotational levels but the extent of depolarization diminishes rapidly with increasing N.

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1. INTRODUCTION

Under thermal conditions nature seems to hide the details of how gas-phase reactions occur through a series of averages—averages over reagent velocity, internal energy, impact parameter, and orientation. To discover the effects of these variables on reactivity, it is necessary to carry out studies of chemical reactions far from equilibrium in which the states of the reactants are more sharply restricted and can be varied in a controlled manner. One class of such experiments involves the use of oriented or aligned reagents to elucidate the role of reactant collision geometry on reaction dynamics [1–5]. Here external fields or

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optical pumping techniques prepare anisotropic distributions of collision partners and the differences in reactivity are measured as the nature of the anisotropy is varied.

Most of the studies conducted to date employ reagents oriented with the aid of external electric or magnetic fields. Examples include salt molecules such as TlF [6–8], CsF [8, 9] and LiF [10], polar symmetric top molecules such as CH_3I [11–21] and CF_3I [12, 22, 23], paramagnetic molecules such as NO [24–30], and H_2 [31, 32] using molecular beam magnetic resonance. An alternative method that might be applied to a wider class of reagents is optical pumping using the polarized output of laser sources. This has been used for some time in the study of nonreactive scattering of aligned or oriented atoms [33] and more recently in the reactive scattering study of aligned atoms or molecules. Examples include the reactions of optically aligned $Ca(^1P)$ with HCl, Cl_2, and CCl_4 [34, 35], the reactions of Xe metastables with IBr aligned by photodissociation [36], collision-induced dissociation of aligned Na_2^+ ions [37], and the reaction of Sr with $HF(v = 1)$ aligned by infrared excitation [38]. The last example is of particular interest. As powerful tunable infrared laser sources become increasingly available, it is expected that this technique might enjoy widespread application.

In optical excitation experiments the absorption process tends to align the angular momentum vector **N** associated with the rotation of the nuclear framework of the molecule, but to leave unaffected any electronic spin **S** or nuclear spin **I** that the molecule might possess. This is a consequence of the spin independence of the electric dipole operator, the weak coupling between these spins and **N**, and the short duration of the excitation process compared to the precession rates of these spins. These spins, which are assumed to have a random spatial distribution, then recouple with **N** to produce a resultant total angular momentum with less spatial alignment than **N**. In this paper we address the role played by such random internal spins in limiting the degree of anisotropy that may be achieved in aligning reagents by optical excitation. The results have immediate application in the design of experiments that use such optically prepared reagents.

For concreteness, we consider a sample of HF molecules aligned through the absorption of linearly polarized infrared light. We assume that the HF molecules in the sample are initially isotropic and that all hyperfine levels (due to the nuclear spin of $\frac{1}{2}$ on both H and F) are coherently excited by a pulse of light. We show that for low values of the rotational quantum number N the depolarization caused by unresolved hyperfine structure is quite severe. However as N is increased, the effects of random internal spin on the degree of alignment rapidly diminish. The final result (formula) developed in this paper is general: (1) it uses the eigenvectors of the molecular hamiltonian expressed in terms of a coupled basis set rather than assuming *a priori* the existence of some hierarchical coupling scheme; (2) it can describe the depolarization of a molecular ensemble having an arbitrary but known spatial anisotropy prepared by means other than optical excitation; and (3) it applies to depolarization by any two random internal spins, not solely nuclear spins. An equivalent formula has been derived by Fano and Macek [39], in terms of uncoupled basis vectors; however, their formula is considerably more cumbersome because it involves multiple summations over magnetic quantum numbers. Expressions correct in the limit that a hierarchical coupling scheme is a valid approximation have also been published [40, 41].

2. THEORY

The origin of hyperfine depolarization may be understood through a simple classical argument. In the case of HF excited by linearly polarized light we assume that the absorption probability depends only on the angle between the rotational angular momentum, **N**, and the electric field vector of the light. Immediately following excitation, the **N** vectors are aligned while the nuclear spins remain randomly oriented. However the nuclear spins couple to **N** to form the total angular momentum **F**, about which all three angular momentum vectors precess. It is the precession of **N** about **F** that decreases the degree of alignment in the excited molecular ensemble. Both the magnitude and time dependence of this precession must be considered. At large values of **N**, we have a situation in which **N** $\approx$ **F**, and the precession may be neglected. Thus only for small values of **N** are the effects of nuclear spin expected to be pronounced. If the precession of **N** about **F** is slow on the timescale of the experiment, nuclear spin may again be neglected. On the other hand, if the precession is rapid, it suffices to calculate a time-averaged depolarization coefficient. However if the precession occurs on the timescale of the experiment, then the alignment must be calculated as a function of time.

While a classical argument is sufficient to illustrate the origin of hyperfine depolarization, quantum mechanics should be used to treat the problem quantitatively. Such a treatment is presented below. We describe the spatial distribution of **N** vectors in terms of the mean values of a set of irreducible tensorial operators $T_q^{(k)}$ [42]. The alignment in a cylindrically symmetric system is commonly designated $\mathscr{A}_0^{(2)}$ where

$$\mathscr{A}_0^{(2)} = \langle (3N_z^2 - \mathbf{N}^2)/\mathbf{N}^2 \rangle \tag{1}$$

has the tensorial quality $k = 2$, $q = 0$.

The quantum mechanical manifestation of the classical precession is an oscillatory variation in $\mathscr{A}_0^{(2)}$ with the time t following the excitation pulse. This temporal variation comes about as follows. The weak coupling between nuclear spin and rotational angular momentum leads to small hyperfine splittings, allowing all hyperfine levels corresponding to a single value of N to be coherently excited when a light pulse is absorbed. (Coherent excitation occurs if $\Delta t \ll 1/\Delta v$ where Δt is the duration of the light pulse and Δv is the splitting between hyperfine levels; this corresponds to a classical situation in which the excitation time is much smaller than the precession time.) The nonrandom phase relations between the various hyperfine levels in the coherently excited molecular ensemble then lead to temporal beats in the expectation value of the alignment operator. The time dependence of $\mathscr{A}_0^{(2)}$ can be determined from the density matrix for the excited molecular ensemble [41]. However the complete density matrix treatment is fairly long [43]. A more succinct approach based on the method of Fano and Macek [39] is possible and will be given here.

In our discussion we adopt the following notation:

N = nuclear rotational angular momentum quantum number.
I_F = nuclear spin of the fluorine atom.
I_H = nuclear spin of the hydrogen atom.
F = total angular momentum quantum number.

F_{int} = an intermediate quantum number formed by coupling $\mathbf{I_F}$ to $\mathbf{N}$. In the limit that a hierarchical coupling scheme is applicable, F_{int} is a good quantum number.

α = an intermediate quantum number that replaces F_{int} when a hierarchical coupling scheme is no longer applicable. In this case, states that diagonalize the hyperfine hamiltonian are labelled by F and α rather than F and F_{int}.

We refer to several theorems concerning angular momentum given by Sobel'man [44] and Fano and Racah [45], using the number given them by the authors prefaced by S or FR.

The time dependence of an operator such as (1) is isolated entirely in the ratio of reduced matrix elements.

$$\langle T_q^{(k)}(t) \rangle = \langle T_q^{(k)}(0) \rangle \frac{(\psi_N \| \exp (iHt/\hbar) T^{(k)}(0) \exp (-iHt/\hbar) \| \psi_N)}{(\psi_N \| T^{(k)}(0) \| \psi_N)}. \tag{2}$$

In writing this relation based on the Wigner–Eckart theorem, it has been assumed that no external fields are present. The hamiltonian is thus a scalar with respect to the total angular momentum of the system, $\mathbf{F}$, and consequently $T_q^{(k)}$ has the same tensorial character as $T_q^{(k)}(0)$ for all t [as is necessary for (2) to be valid] [46]. The time dependent ratio of reduced matrix elements in equation (2) is commonly referred to as a *perturbation coefficient* and denoted $G^{(k)}(t)$. In order to evaluate this expression we first apply S(14.66) twice. This yields, after inversion,

$$(I_H \| I_H^{(0)} \| I_H)(I_F \| I_F^{(0)} \| I_F)(N \| T^{(k)}(t) \| N)$$

$$= \sum_{F_{int}, F_{int'}, F, F'} (I_H(I_F N)F_{int} F \| I_H^{(0)} I_F^{(0)} T^{(k)}(t) \| I_H(I_F N)F_{int}' F')$$

$$\times ((I_H I_H)0(F_{int} F_{int}')k \,|\, (I_H F_{int})F(I_H F_{int}')F')^{(k)}$$

$$\times ((I_F I_F)0(NN)k \,|\, (I_F N)F_{int}(I_F N)F_{int}')^{(k)}. \tag{3}$$

Here we have introduced unit operators for the spin degrees of freedom, $I_H^{(0)}$ and $I_F^{(0)}$, and the Heisenberg-representation form for the time-dependent operator (acting only on $\mathbf{N}$),

$$T^{(k)}(t) = \exp (iHt/\hbar) T^{(k)}(0) \exp (-iHt/\hbar). \tag{4}$$

Equation (3) is simply an evaluation of the reduced matrix elements in the coupled representation $|I_H(I_F N)F_{int} F)$, according to the scheme $\mathbf{I_F} + \mathbf{N} = \mathbf{F_{int}}$, $\mathbf{I_H} + \mathbf{F_{int}} = \mathbf{F}$. Because H is a scalar, two applications of FR(15.15) yield

$$(I_H(I_F N)F_{int} F \| \exp (iHt/\hbar) B^{(k)} \exp (-iHt/\hbar) \| I_H(I_F N)F_{int}' F')$$

$$= \sum_{F_{int}'', F_{int}'''} \frac{(I_H(I_F N)F_{int} F \| \exp (iHt/\hbar) \| I_H(I_F N)F_{int}'' F)}{(2F + 1)^{1/2}}$$

$$\times (I_H(I_F N)F_{int}'' F \| B^{(k)} \| I_H(I_F N)F_{int}''' F')$$

$$\times \frac{(I_H(I_F N)F_{int}''' F' \| \exp (-iHt/\hbar) \| I_H(I_F N)F_{int}' F')}{(2F' + 1)^{1/2}} \tag{5}$$

where we set $B^{(k)} \equiv I_H^{(0)} I_F^{(0)} T^{(k)}(0)$.

Next the reduced matrix elements of $\exp (iHt/\hbar)$ are evaluated by finding the representation in which the hamiltonian is diagonal. They become ordinary

matrix elements according to

$$(I_H(I_F N)F_{int}F\|\exp(iHt/\hbar)\|I_H(I_F N)F'_{int}F)/(2F+1)^{1/2}$$

$$= (I_H(I_F N)F_{int}FM_F|\exp(iHt/\hbar)|I_H(I_F N)F'_{int}FM_F), \quad (6)$$

which can be evaluated for *any* value of M_F. In terms of the eigenvalues $E_{\alpha F}$ and the eigenvectors

$$C^{(F)}_{F_{int},\alpha} \equiv (I_H(I_F N)F_{int}FM_F|(I_H I_F N)\alpha FM_F)$$

obtained from diagonalization of H, equation (6) may be written as

$$(I_H(I_F N)F_{int}F\|\exp(iHt/\hbar)\|I_H(I_F N)F'_{int}F)/(2F+1)^{1/2}$$

$$= \sum_\alpha C^{(F)}_{F_{int},\alpha} \exp(iE_{\alpha F}t/\hbar)C^{(F)*}_{F_{int},\alpha'}. \quad (7)$$

The last step is to use the inverse of equation (3) to simplify the reduced matrix elements of $B^{(k)}$ in equation (5);

$$(I_H(I_F N)F''_{int}F\|I_H^{(0)}I_F^{(0)}T^{(k)}(0)\|I_H(I_F N)F'''_{int}F')$$

$$= (I_H\|I_H^{(0)}\|I_H)(I_F\|I_F^{(0)}\|I_F)(N\|T^{(k)}(0)\|N)$$

$$\times ((I_H I_H)0(F''_{int}F'''_{int})k|(I_H F''_{int})F(I_H F'''_{int})F')$$

$$\times ((I_F I_F)0(NN)k|(I_F N)F''_{int}(I_F N)F'''_{int})^{(k)}. \quad (8)$$

Putting all the factors together, and using the general relation

$$((II)0(NN')k|(IN)F(IN')F')^{(k)}$$

$$= \left[\frac{(2F+1)(2F'+1)}{(2I+1)}\right]^{1/2}(-1)^{I+k+N'+F}\begin{Bmatrix}N' & F' & I \\ F & N & k\end{Bmatrix}, \quad (9)$$

yields the result

$$G^{(k)}(t) = \sum_{\alpha,\alpha',F,F'} \frac{(2F+1)(2F'+1)}{(2I_H+1)(2I_F+1)}\cos[(E_{\alpha F}-E_{\alpha'F'})t/\hbar]$$

$$\times \left|\sum_{F_{int},F'_{int}}(-1)^{F_{int}+F_{int'}}(2F_{int}+1)^{1/2}(2F'_{int}+1)^{1/2}C^{(F)}_{F_{int},\alpha}C^{(F')*}_{F_{int},\alpha'}\right.$$

$$\times \begin{Bmatrix}F_{int} & N & I_F \\ N & F_{int} & k\end{Bmatrix}\begin{Bmatrix}F_{int} & F' & I_H \\ F & F_{int} & k\end{Bmatrix}\Bigg|^2. \quad (10)$$

It can be easily verified using sum rules for the 6*j*-coefficients and the orthonormality of the eigenvectors that $G^{(k)}(0) = 1$, as expected.

We obtain the time-averaged perturbation coefficient by removing all terms in which $E_{\alpha F} \neq E_{\alpha'F'}$ in equation (10); ignoring the possibility of degenerate energy eigenvalues this results in

$$\bar{G}^{(k)} = [(2I_F+1)(2I_H+1)]^{-1}\sum_{\alpha,F}(2F+1)^2$$

$$\times \left|\sum_{F_{int},F_{int'}}(-1)^{F_{int}+F_{int'}}[(2F_{int}+1)(2F'_{int}+1)]^{1/2}\right.$$

$$\times C^{(F)}_{F_{int},\alpha}C^{(F)*}_{F_{int},\alpha'}\begin{Bmatrix}F'_{int} & N & I_F \\ N & F_{int} & k\end{Bmatrix}\begin{Bmatrix}F'_{int} & F & I_H \\ F & F_{int} & k\end{Bmatrix}\Bigg|^2. \quad (11)$$

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In the limit of a hierarchical coupling scheme F_{int} becomes a good quantum number and equation (10) can be simplified using

$$C^{(F)}_{F_{int}, \alpha} = \delta_{\alpha, F_{int}} \tag{12}$$

to yield

$$G^{(k)}(t) = [(2I_F + 1)(2I_H + 1)]^{-1} \sum_{F, F', F_{int}, F'_{int}}$$

$$\times (2F + 1)(2F' + 1)(2F_{int} + 1)(2F'_{int} + 1) \begin{Bmatrix} F'_{int} & N & I_F \\ N & F_{int} & k \end{Bmatrix}^2$$

$$\times \begin{Bmatrix} F'_{int} & F' & I_H \\ F & F_{int} & k \end{Bmatrix}^2 \cos \left[(E_{F_{int}, F} - E_{F'_{int}, F'})t/\hbar \right]. \tag{13}$$

3. ALIGNMENT OF HF($v = 1$, N): AN EXAMPLE

For an isotropic distribution of molecules excited by a pulse of linearly polarized light, the excited state anisotropy may be described solely in terms of the alignment parameter $\mathscr{A}_0^{(2)}$ whose time dependence is simply given by

$$\mathscr{A}_0^{(2)}(t) = \mathscr{A}_0^{(2)}(t = 0)G^{(2)}(t). \tag{14}$$

Thus the alignment at time t requires a calculation of the initial alignment at $t = 0$ and the perturbation coefficient $G^{(2)}(t)$. We illustrate this procedure for the infrared-allowed transition HF($v'' = 0$, N'') → HF($v = 1$, N).

Under the action of linearly polarized excitation the probability of a particular (N'', M'') → (N, M) transition is proportional to the square of the Clebsch–Gordan coefficient $\langle N''M'', 10 | NM \rangle$. Hence according to equation (1) the initial alignment may be found from

$$\mathscr{A}_0^{(2)}(t = 0) = \frac{\sum_M [3M^2 - N(N + 1)]\langle N''M, 10 | NM \rangle^2}{N(N + 1) \sum_M \langle N''M, 10 | NM \rangle^2}. \tag{15}$$

This expression readily reduces to the analytic form [47, 48]

$$\mathscr{A}_0^{(2)}(t = 0) = -\frac{2}{5} + \frac{3}{5(N + 1)} \tag{16}$$

for a P branch transition ($N = N'' - 1$) and

$$\mathscr{A}_0^{(2)}(t = 0) = -\frac{2}{5} - \frac{3}{5N} \tag{17}$$

for an R branch transition ($N = N'' + 1$).

For large N, equations (16) and (17) show that $\mathscr{A}_0^{(2)}(t = 0)$ approaches the classical limit of minus two-fifths, independent of the excitation branch. However, for low to moderate values of N, it is seen that excitation via the R branch always creates a larger initial alignment than the corresponding P branch excitation that connects to the same final N value. Indeed, in the absence of other effects, the maximum alignment is for the $R(0)$ line ($N = 1$) for which $\mathscr{A}_0^{(2)}(t = 0) = -1$.

To gauge how these conclusions are modified by the presence of hyperfine structure a computer program has been written to find the perturbation coefficient $G^{(2)}(t)$ by evaluating equation (10). This program uses the vibration–rotation hyperfine structure information available from the frequency-stabilized (~ 1 kHz) colour centre laser studies on HF by Breant *et al.* [49]. This ultra high resolution study shows that vibrational excitation alters significantly the hyperfine structure constants compared to their ground state values [50]. The figure displays the perturbation coefficients $G^{(2)}(N, t)$ for $N = 1$–3 and 10. As a consequence of equation (14), it is seen that $\mathscr{A}_0^{(2)}(t)$ varies periodically with t. This behaviour is caused by the coupling of $\mathbf{N}$ with the nuclear spins $\mathbf{I}_H$ and $\mathbf{I}_F$. During excitation $\mathbf{N}$ acquires a certain alignment (its maximum value) while the nuclear spins $\mathbf{I}_H$ and $\mathbf{I}_F$ remain unaffected. Because of hyperfine coupling there is a transfer of alignment between the different angular momenta. The resultant of $\mathbf{I}_H$ and $\mathbf{I}_F$ becomes aligned with a consequent loss of alignment of $\mathbf{N}$. This exchange of alignment continues in a periodic and reversible manner, $\mathscr{A}_0^{(2)}(t)$ oscillating about its maximum and minimum values in a complex fashion for this system of two random spins. As expected, the hyperfine depolarization is seen to be quite pronounced at low values of N but to decrease rapidly with increasing N. Although the $G^{(2)}(N, t)$ were calculated using the exact HF molecular eigenvectors, the coupling in HF is such that a very good approximation is obtained if equation (13) is used and $\mathbf{N}$ is assumed to couple first to $\mathbf{I}_F$ and the resultant to couple then to $\mathbf{I}_H$.
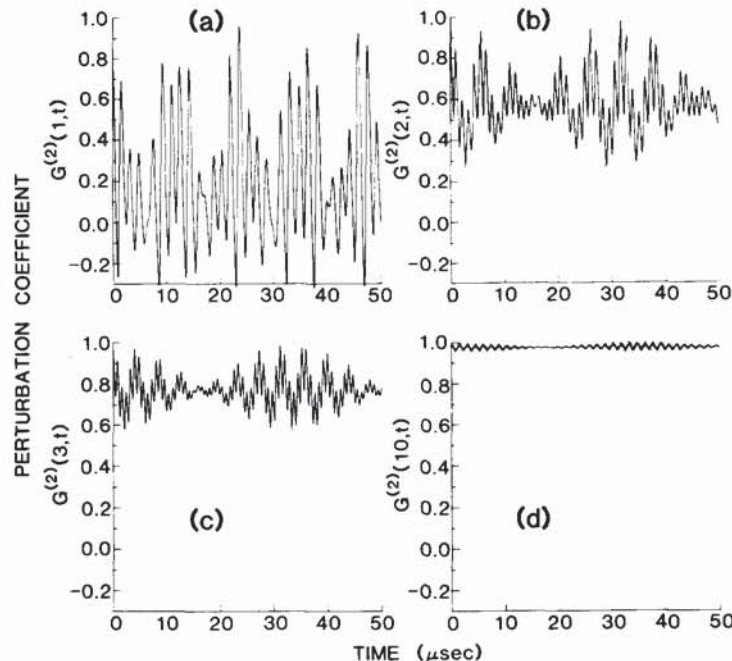
Time-dependent behaviour of the perturbation coefficients $G^{(2)}(N, t)$, $N = 1$–3 and 10, for HF($v = 1$, N), evaluated using equation (10). The perturbation coefficient $G^{(2)}(N, t)$ describes the time evolution of the alignment $\mathscr{A}_0^{(2)}(N)$ in the rotational level N under the influence of the hyperfine interaction between $\mathbf{N}$ and the two randomly oriented nuclear spins $\mathbf{I}_H$ and $\mathbf{I}_F$.

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N	$\mathscr{A}_0^{(2)}(0)$	$\bar{G}^{(2)}$	$\bar{\mathscr{A}}_0^{(2)}$
1	$-1{\cdot}00$	$0{\cdot}195$	$-0{\cdot}195$
2	$-0{\cdot}70$	$0{\cdot}574$	$-0{\cdot}402$
3	$-0{\cdot}60$	$0{\cdot}768$	$-0{\cdot}461$
4	$-0{\cdot}55$	$0{\cdot}857$	$-0{\cdot}471$
5	$-0{\cdot}52$	$0{\cdot}903$	$-0{\cdot}470$
10	$-0{\cdot}46$	$0{\cdot}973$	$-0{\cdot}448$

Initial alignment, time-averaged depolarization coefficient, and time-averaged alignment for various values of N for $HF(v = 1, N)$ following linearly polarized pulsed R branch excitation.

For many experiments the important quantity is not $\mathscr{A}_0^{(2)}(t)$ but rather the time-averaged alignment. The table lists the values $\bar{\mathscr{A}}_0^{(2)}(N)$ for $N = 1{-}5$ and $N = 10$ in the case of R branch excitation. For $HF(v = 1, N)$ it is concluded that only excitation via the $R(0)$ line leads (ironically) to poor HF average alignment due to hyperfine depolarization, while excitation by the other members of the R branch creates an excited state alignment close to the limiting classical value of $-0{\cdot}4$.

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[40] See reference [39]. There is apparently a misprint in this paper. The first $6j$ symbol in their equation 40 should read

$$\begin{Bmatrix} F' & F & k \\ J & J' & I \end{Bmatrix}.$$

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[46] Strictly speaking, for equation (2) to be valid, H should be a scalar with respect to **N** as well as for **F**, which is not true here. However, since the spins are initially randomly oriented, since $T_q^{(k)}(0)$ does not act on the spins, and since there is an implied trace over the spin magnetic quantum numbers, the combination $\exp(iHt/\hbar) \ldots \exp(-iHt/\hbar)$ is in fact a scalar with respect to **N**.

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