Chemically Induced Dynamic Nuclear Polarization In Systems Containing Large Hyperfine Coupling Constants

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Nuclear spin polarization effects induced in radical pairs with one or more strong $^{13}$C hyperfine coupling constants have been evaluated. The pairs were generated by photoinduced $\alpha$-cleavage or hydrogen abstraction reactions of carbonyl compounds. Several examples illustrate how changes in the magnetic field strength ($H_0$) and the $g$-factor difference ($\Delta g$) affect the general appearance of the resulting CIDNP multiplets. The results bear out an earlier caveat concerning the qualitative interpretation of CIDNP effects observed for multiplets.

Introduction

Chemically induced dynamic nuclear polarization (CIDNP) effects have been shown to be quite useful for investigating a variety of organic reaction mechanisms. These effects are generated by hyperfine-induced inter-system crossing in radical or radical-ion pairs and can be transferred to neutral diamagnetic products, if the pairs are involved in competing electron spin selective reactions. These observed effects can be divided into two categories: net effects, which are usually observed when the $g$-factor difference between the two radicals is sizable, or multiplet effects, which are observed typically when the $g$-factor difference is negligible. The use of these effects in mechanistic assignments has been greatly aided by the development of qualitative sign rules, originally proposed by Kaptein, which allow the prediction of CIDNP effects on the basis of characteristic parameters of the radical pair (spin multiplicity), the individual radicals (hyperfine coupling constants (hfc), electron $g$ factors), the products ($J$ coupling), and the mechanism of product formation. Alternatively, the observed effects can be utilized to assign one of these parameters, if the remaining parameters are known.

Several years ago, we and others called attention to a third general case of polarization, which is realized when both a sizable $g$-factor difference and a sizable hyperfine coupling constant are present along with other, smaller hyperfine coupling constants. In these cases, multiplet effects may be observed for the nuclei with the lower hfc's even for relatively large $g$-factor differences. These effects are of particular interest, because the less pronounced effects, the net effects superimposed on strong multiplet effects, were found to violate Kaptein's rules. Typical examples include the effects induced in radical pairs containing $^{13}$Cbenzoyl or other $^{13}$Cacyl radicals. These pairs can be generated conveniently by the $\alpha$-cleavage of photoexcited ketones, for example, by the photolysis of dibenzyl ketone or benzoin.

The relative polarization intensities of the two lines comprising an NMR doublet are determined in essence by the difference in the electron precession frequencies, $\omega_c$, of the two radicals. For a two-spin AX system, the intensities of the A doublet are given by

$$I_{A1} = \pm [\omega_{A1}^{1/2} - \omega_{A2}^{1/2}]$$

and

$$I_{A2} = \pm [\omega_{A2}^{1/2} - \omega_{A1}^{1/2}]$$

The frequency difference is a function of the difference in the Zeeman energies of the two radicals and on the hfc's of the two nuclei

$$\omega_{A1} = \frac{\gamma g_0\hbar}{2}(\Delta g_0 H_0/g \pm \gamma d_A + \gamma d_X)$$

and

$$\omega_{A2} = \frac{\gamma g_0\hbar}{2}(\Delta g_0 H_0/g \pm \gamma d_A - \gamma d_X)$$

The relative intensities of the lines can be evaluated and displayed as a function of $\Delta g_0 H_0$ for particular values of $\omega_c$ and $\omega_A$, on the basis of a formalism developed by Muller for the graphical analysis of CIDNP spectra. To obtain more general results, independent of a particular hyperfine coupling $d_A$, we have modified this method by plotting the signal intensities as a function of a parameter $G = \Delta g_0 H_0/d_A$. This approach yields a characteristic pair of intensity curves for a given ratio of $d_A$ to $d_X$.

In order to probe the range of these effects, the magnetic field strength, $H_0$, or the $g$-factor difference, $\Delta g$, can be varied more or less conveniently. On the other hand, it is difficult to vary the hyperfine coupling in a rational and predictable manner. In order to vary $H_0$, the experiments can be carried out in different NMR spectrometers operating at different magnetic field strengths, or the radical-pair reaction can be carried out in a secondary magnet, whose field can be varied, and the induced polarization measured after rapid transfer to a spectrometer of constant field. Alternatively, the $g$-factor difference of the pair could be altered by chemically modifying one of the radicals. In this paper, we report examples of both types of modifications: we compare CIDNP effects induced during photoreactions of $^{13}$C-labeled carbonyl compounds.

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compounds at field strengths of 21 and 58.3 kG (corresponding to \(^{1}H\) frequencies of 90 and 250 MHz, respectively); and we vary the \(2g\) value of a given pair, by introducing suitable substituents in appropriate positions of one of the radicals or by replacing one of the radicals of the pair.

**Experimental Section**

Typical samples used in this study contained (2–4) \(\times 10^{-2}\) M of an aldehyde or ketone in solvents such as acetone-\(d_6\) (Aldrich Gold Label), acetonitrile-\(d_3\) (Merck, Sharp, and Dohme; 99%), cyclohexane-\(d_2\) (Aldrich; 99.5% \(D\)), or chloroform-\(d\) (Aldrich; Gold Label), acetonitrile-\(d_3\) (Merck, Sharp, and Dohme; 99%), of an aldehyde or ketone in solvents such as acetone-\(d_6\) (Aldrich; Gold Label), acetonitrile-\(d_3\) (Merck, Sharp, and Dohme; 99%), or chloroform-\(d\) (Aldrich; Gold Label), acetonitrile-\(d_3\) (Merck, Sharp, and Dohme; 99%), or chloroform-\(d\) (Aldrich; Gold Label). The samples were deoxygenated by purging with a stream of clean, dry argon for 5 min and were irradiated in the probe of the NMR spectrometer. The experiments performed at 21 kG employed a Bruker WH 90 Fourier transform NMR spectrometer with a 1000-W Hanovia high-pressure mercury lamp as a light source. A Bruker AF 250 NMR spectrometer was used for the experiments at 58.3 kG; an ILC Technologies 300-W high-pressure xenon lamp fitted with a water filter served as the light source. In this case, the radiation was guided to the sample with a specially constructed Suprasil light pipe. A pulse angle of 15° was employed to minimize the distortion of the expected multiplet effects. The number of scans was chosen so as to produce satisfactory signal-to-noise ratios. The acquisition time was \(\sim 5\) s/pulse with a relaxation delay of 0.5 s. Depending on the number of scans, the total time required for the experiment varied from 100 to 500 s. During the irradiation, time depletion of the ketones was noticeable (5–20%). This introduced an uncertainty into the assignment of the CIDNP enhancements for the substituted di-4-Methoxydibenzyl ketone-\(^{13}\)CO (90%) was synthesized according to a procedure developed in the literature.\(^{26}\) The product was purified by flash chromatography with 5% ether in hexane. The overall yield was \(\sim 35\%\) based on labeled phenylacetic acid.

**Materials**

*Deoxybenzoin-\(^{13}\)CO (90%)* (1,3-diphenylacetone-\(^{13}\)CO) was synthesized by reaction of benzylimagnesium chloride with phena-4-Chlorodibenzyl ketone-\(^{13}\)CO (99%) was synthesized by reaction of benzylmagnesium chloride (Alfa) with benzoic acid-\(^{13}\)CO (Aldrich) according to the procedure used for the preparation of 4-chlorodibenzyl ketone-\(^{13}\)CO.\(^{27}\) The product was purified by flash chromatography with 5\% ether in hexane. The overall yield was \(\sim 35\%\) based on labeled phenylacetic acid.

*Deoxybenzoin-\(^{13}\)CO (90%)* was synthesized according to a method described in the literature.\(^{25}\) The product was purified by flash chromatography with 5\% ether in hexane.

*4-Chlorodibenzyl ketone-\(^{13}\)CO (99%)* (KCl-CN (2.5 mmol, 99% \(^{13}\)C; Aldrich) was placed in a round-bottom flask containing 30 mL of 95\% ethanol, and 2.5 mmol of 4-chlorobenzyl chloride (Aldrich) was added. The mixture was refluxed for 30 h\(^{28}\) and the solution extracted with two 30-mL portions of methylene chloride. The organic layer was washed twice with water and dried over magnesium sulfate, and the solvent was evaporated. The resulting 4-chlorobenzyl cyanide was obtained in \(\sim 95\%\) yield.

Phenylmagnesium chloride (Aldrich; 5 mmol) was placed in a round-bottom flask containing 20 mL of dry ether, the solution was purged with argon, and an ether solution of the above 4-chlorobenzyl cyanide (99% \(^{13}\)CN, used without further purification) was added dropwise.\(^{25}\) (No product was observed when the Grignard solution was added to the cyanide solution!) The mixture was refluxed for 12 h, 20 mL of 5\% aqueous \(\text{H}_2\text{SO}_4\) was added to the refluxing solution, and the reaction mixture was allowed to cool and filtered for 40 min to complete the hydrolysis of the resulting imine. The quenched solution was extracted with two 30-mL portions of ether, and the ether phase was washed twice with water and then dried over magnesium sulfate. The resulting 4-chlorodeoxybenzoin (\(^{13}\)CO, 99%) was recrystallized from a 2\% ether/hexane solution and obtained in an overall yield of \(\geq 85\%\) based on KCl-CN.

*4-Chlorodibenzyl ketone-\(^{13}\)CO (99%)* was synthesized by reaction of benzylimagnesium chloride (Alfa) with benzoic acid-\(^{13}\)CO (Aldrich) according to the procedure developed in the literature. The compound was purified by flash chromatography with 5\% ether in hexane. The resulting ketone (99% \(^{13}\)CO) was obtained in \(\geq 50\%\) yield based on KCl-CN.

**Results and Discussion**

The first case to be discussed here involves the photolysis of 1,3-diphenylacetone. The triplet state of this ketone undergoes a-cleavage, generating a benzyl radical paired with a phenylacetyl radical (pair A):

\[
\begin{align*}
\text{hv} & \rightarrow \\
\text{R} & \quad \text{R} \\
\text{O} & \quad \text{CH}_2
\end{align*}
\]

This pair has a sizable \(g\)-factor difference \((g_1 = 2.0026, g_2 = 2.0008, \Delta g = 0.0018)^{28}\) and two substantially different hyperfine coupling constants \(\alpha_0 = 122.3 \text{ G}, \alpha_0 = -16.3 \text{ G}, \alpha_1/\alpha_0 = 7.5^{28,29}\). Photolysis of the unlabeled compound was shown to result in emission for the benzyllic signal, whereas the \(^{13}\)CO-labeled ketone, at a field strength of 90 MHz, gives rise to an absorption/emission (A/E) multiplet effect, in which the absorption component is slightly larger (Figure 1, top right).

For the system under consideration, the intensities are predicted to show the field dependence illustrated in Figure 2. It is clear that at a sufficiently high field the multiplet effect should give way to an (unexceptional) net effect. However, the experiment at 250 MHz falls short of this expectation, as the observed effect retains a decided multiplet effect even to an even more pronounced "anti-Kaptein" net effect (Figure 1, top left). A more detailed
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chosen (or available) for the experiments. The figure shows that the ylacetyl radical (a of the condition
Figure 2. Relative polarization calculated for the proton signals of diphenylacetone generated from radical pair A, with a 13CO-labeled phenylacetyl radical (a 13C-H spin system with %G = 124 G, %G = -16 G, %G/%G = 7.5) as a function of the parameter %G = %G/θ/θ. The values of %G for 21 and 58.3 kG are indicated by vertical lines.

inspection of Figure 2 reveals that the seeming lack of field dependence is but an artifact of the two magnetic field strengths chosen (or available) for the experiments. The figure shows that multiplet effects are expected for a wide range of magnetic field, defined by the condition

\[ H_0 = ±a_c/Δg \]  

(5)

They pass through an extreme anti-Kapteijn net effect, before reaching the domain where both lines obey Kapteijn's net effect rule. For the system on hand, given the 13C and 1H hyperfine couplings of the phenylacetyl and benzyl radicals, respectively, the field strength of 58.3 kG, corresponding to a 1H frequency of 250 MHz (and to %G = 6.8) lies relatively close to the expected “crossover” point, %G = 7.5. This value could be reached by increasing either the magnetic field to a value of 68.8 kG (295 MHz) or the g-factor difference of the radical pair to a value of ~0.0021.

Accordingly, it appeared possible to accomplish the crossover by chemically modifying one of the constituent radicals of pair A. In particular, appropriate modification of the benzyl radical should result in a slightly larger g-factor difference; correspondingly, a lower field strength should be required for the crossover. The electron g-factors of benzyl radicals can be altered by introducing appropriate substituents in the α, ortho, or para position. Compared to the benzyl radical (g = 2.0026) the p-methoxybenzyl (g = 2.00273, %G = 0.00193) and the p-chlorobenzyl radicals (g = 2.00135, %G = 0.00235) have slightly higher electron g-factors, corresponding to calculated crossover field strengths (H0 = GC × aG/Δg = GC/Δg) of 64 and 52 kG and 1H frequencies of 275 and 226 MHz, respectively. These considerations suggest that the system consisting of a p-chlorobenzyl paired with a benzoyl radical should achieve the crossover in the higher field spectrometer. On the other hand, the corresponding pair containing a p-methoxybenzyl radical should fall short of the crossover region. Accordingly, the chloro and methoxy derivatives were synthesized, and their photoinduced CIDNP effects were studied in the 58.3-kG spectrometer at a 1H frequency of 250 MHz.

The polarization observed for these monosubstituted ketones is complicated by the fact that the substrates contain two different carbonyl-benzyl bonds, which are apparently cleaved essentially randomly. Therefore, two radical pairs are generated in each case: one containing the para-substituted benzyl radical and having an increased Δg (pairs A1, A3), the other containing instead a para-substituted phenylacetyl radical (pairs A2, A4). Since the

\[ \text{PAIR A}_1 \quad \text{PAIR A}_2 \]

chlorine or methoxy substituents in the latter occupy a position without appreciable spin density, the g factors of these radicals and, consequently, the magnetic parameters of the pairs are essentially identical with those of pair A. For both substrates, the chemical shifts of the two types of benzyl protons are sufficiently different so that the respective polarizations can be observed without distortion due to overlapping signals.

The CIDNP spectra observed for the benzylic doublets of p-methoxybenzyl ketone (Figure 1, bottom left) are not very satisfactory. The polarization is relatively weak and partially obscured by a modest degree of line broadening. Although it is difficult to determine the correct intensities for the four lines objectively, visual comparison of the spectra observed in the dark and during irradiation suggests an overall A/E multiplet effect. The observed patterns suggest that the radical pairs derived from this ketone fall short of the crossover region, as expected.

In contrast, the CIDNP effects observed during the photolysis of p-chlorodibenzo ketone clearly document that the corresponding radical pairs, A' and A'', fall into two different regions. The two benzylic doublets show substantially different polarization patterns: one pair shows the pronounced multiplet effect characteristic for the parent ketone, whereas the other exhibits a pure net effect (Figure 1, bottom right). This dramatic effect caused by a relatively subtle change in the Δg parameter is precisely the change predicted by the radical-pair theory of CIDNP as well as by the approximate solution provided by the graphic method discussed above.

Another, closely related, acyl-benzyl radical pair (pair B) can be obtained by photolysis of deoxybenzoin.31

\[ \text{PAIR B} \]

The resulting pair has a sizable g-factor difference (g = 2.0026, g = 2.0008, Δg = 0.0018)12 and substantially different hyperfine coupling constants (%GC = 128.2 G,13 aH = -16.3 G, %GC/aH = 7.9). The intensity curves predicted for the 1H doublet of the recombination product (Figure 3) are very similar to those of pair A; the ratio of carbon to proton hyperfine coupling corresponds to a crossover %G value of 7.9. The CIDNP effects observed during photolysis of 13C-O-labeled deoxybenzoin (Figure 4, left) show a pronounced A/E multiplet effect, even at 250 MHz. In view of the excellent agreement between prediction and experiment encountered for pair A (vide supra), it is noteworthy that the


4.1 4.0

Figure 4. $^1$H polarization (of benzylic protons only) observed during irradiation of deoxybenzoin-$^{13}$CO (left) and $p$-chlorodeoxybenzoin-$^{13}$CO (right) in cyclohexane-$d_{12}$ at 250 MHz.

7.0 6.0 5.0 6.0 5.5 4.7 3.5

Figure 5. Top: Relative polarization of the proton signals of a $^{13}$C-$^1$H spin system calculated according to the radical-pair theory with $a_c/a_H = 8.7$ as a function of the parameter $G = \Delta g_{HH}/a_H$. Dashed bars are placed at the values for 21 and 58.3 kG for pair C containing a benzoyl-$^{13}$CO radical; solid bars are placed at values of $G' = G \pm a_c/a_H$ for pair C containing both benzoyl-$^{13}$CO and hydroxybenzyl-$^{13}$COH radicals. Because of the sign of the large $^{13}$COH-$^1$H coupling, decreasing values of $G$ are plotted to the right. Bottom: $^1$H polarization observed for the benzylic protons of benzoin-$^{13}$CO and hydroxybenzyl-$^{13}$COH during the irradiation of benzaldehyde-$^{13}$CO in cyclohexane-$d_{12}$. The left pair of doublets was recorded at 90 MHz whereas the right pair was observed at 250 MHz. The absorption singlet denoted by an asterisk represents the downfield signal for the benzyl protons of $\alpha$-phenylcyclohexylmethanol-$d_{11}$ (vide infra).

relative intensities generated in pair B differ substantially from the predicted ones. The photolysis of $^{13}$C-O-labeled $p$-chlorodeoxybenzoin also gave rise to benzylic polarization of overall multiplet character (Figure 4, right). However, in this case, both signals appear in emission. Obviously, the change in $\Delta G$ is sufficient to reach the region where the net effect can be interpreted with confidence.

A third radical pair, closely related to both pairs A and B, can be generated by photolysis of benzoin and, independently, by reaction of photoexcited with ground-state benzaldehyde.

Figure 6. Top: Relative polarization of the proton signals of a $^{13}$C-$^1$H spin system calculated for pair D containing a hydroxybenzyl-$^{13}$COH radical ($a_c = 23$ G, $a_H = -14.9$ G, $|a_c/a_H| = 1.5$) as a function of the parameter $G = \Delta g_{HH}/a_H$. The shaded area indicates the range of $G$ values calculated for $0.0004 < \Delta G < 0.0005$ at fields of 21 (right) and 58.3 kG (left). Bottom: $^1$H polarization observed for the benzylic protons of $\alpha$-phenylcyclohexylmethanol-$d_{11}$ during the irradiation of benzaldehyde-$^{13}$CO in cyclohexane-$d_{12}$ at 250 MHz (left) and 90 MHz (right). The A/E multiplet denoted by asterisks represents the upfield benzylic doublet of benzoin-$^{13}$CO,$^{13}$COH (vide supra).

Figure 7. $^1$H polarization observed for the benzylic protons of benzoin-$^{13}$CO,$^{13}$COH (left) and phenyl(trichloromethyl)methanol-$^{13}$COD during irradiation of benzaldehyde-$^{13}$CO in chloroform-$d$ (right) at 250 MHz.

The radical pair produced in these reactions (pair C) has an increased g-factor difference ($\Delta g = 0.0025$) and, once again, substantially different hyperfine coupling constants ($a_c = 128.2$ G, $a_H = -14.9$ G, $a_c/a_H = 8.7$). When pair C is generated by irradiation of $^{13}$C-O-labeled benzaldehyde, the resulting benzoin molecule contains two $^{13}$C nuclei and its $^1$H spectrum shows a doublet of doublets with $J_{CH} = 145.3$ Hz and $J_{CH} = -3.1$ Hz. At 90 MHz, both doublets show pronounced A/E multiplet effects (Figure 5). However, when irradiation is carried out at 250 MHz, only the downfield doublet shows this type of multiplet effect, whereas the upfield doublet shows net polarization. The four different doublets observed at two different magnetic field strengths agree exceedingly well with the intensities ap-

proximated by the graphic method on the basis of eq 1 and 2. The examples discussed so far illustrate the following: (1) how variations in the magnetic field strength affect the general appearance of a CIDNP multiplet and (2) how changes in g-factor differences brought about by substituents affect the polarization of a multiplet. It remains to consider variations of Ag by exchanging one constituent of a radical pair. For this purpose, we have studied hydrogen (deuterium) abstraction reactions of photoexcited benzaldehyde with three additional substrates: cyclohexane-d$_{12}$, methylene-d$_2$ chloride, and chloroform-d.

The light-induced abstraction reactions from these substrates occur in competition with the self-reaction of benzaldehyde, generating radical pairs in which the benzoyl radical (g = 2.0083)$^{28}$ and trichloromethyl (g = 2.0091)$^{36}$ are replaced successively by cyclohexyl (g = 2.0026)$^{35}$ di-chloromethyl (g = 2.0083)$^{28}$ and trichloromethyl (g = 2.0091)$^{36}$.

In each of the resulting radical pairs, the $^{13}$C and $^1$H hyperfine coupling constants of the hydroxybenzyl radical determine the polarization observed for a coupling product which is, however, modified by the changing g-factor difference for the different counterradicals. The ratio of hyperfine couplings is small (l$e$/a$_{1H}$ = 1.5) whereas the g-factor difference varies from small (−0.0004 < Δg < −0.0005) for cyclohexyl to very large (+0.0060) for trichloromethyl. The radical pair with the small g-factor difference (pair D) gives rise to a nearly pure A/E multiplet effect at 21 kG and to net emission, on which a strong A/E multiplet effect is superimposed, at 58.8 kG (Figure 6).

In contrast, the photo reactions with methylene-d$_2$ chloride and chloroform-d gives rise to radical pairs with substantially larger g-factor differences and, accordingly, to pure net effects. For these pairs, enhanced absorption is observed, in keeping with the sign change of the g-factor difference. This is illustrated in Figure 7 for the hydrogen abstraction from chloroform.

**Conclusion**

The results presented in this paper lead to one overriding conclusion: the presence of strongly (hyperfine) coupled nuclei (most often $^{13}$C) in a radical pair profoundly influences the CIDNP effects of nuclei (most often $^1$H) that are (J) coupled to the former in products resulting from that pair. As previously indicated, CIDNP effects observed in such cases can be interpreted only with caution. In particular, Kaptein's sign rules can be applied only to the “major” effects, i.e., to the net effect, when both signals have the same direction, and to the multiplet phase, when the signals have opposite directions.

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**Registry No.** 4-Methoxydibenzyl ketone-13CO, 121329-44-0; deoxybenzoin-13CO, 104917-39-7; 4-chlorodeoxybenzoin-13CO, 121329-45-1; dibenzyl ketone-13CO, 68120-92-3; 4-chlorodibenzyl ketone-13CO, 121329-46-2; 1,3-diphenylacetone, 102-04-5; benzaldehyde, 100-52-7; cyclohexane-d$_{12}$, 1735-17-7; chloroform-d, 865-49-6; methylene-d$_2$ chloride, 1665-00-5; deuterium, 7782-39-0.

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**Determination of Excited-State Rotational Constants and Structures by Doppler-Free Picosecond Spectroscopy**

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Picosecond time-resolved fluorescence measurement of purely rotational coherence is developed as a Doppler-free technique for the determination of rotational constants of large molecules in their excited states. We present detailed analyses of purely rotational coherence measurements, supplying new information about the rotational constants and structures of the first excited electronic states of t-stilbene, four t-stilbene van der Waals complexes, and anthracene, including values for all three anthracene S$_0$ rotational constants. Evidence is considered in the case of stilbene for a transition dipole with a significant component perpendicular to the $a$ inertial axis, and the consequences of such a dipole are explored by way of numerical simulations. Excited-state structures are proposed for stilbene and stilbene-rare-gas complexes and comparisons made with model calculations of the van der Waals potential. Application of the new spectroscopic technique to molecules of large asymmetry is demonstrated by the analysis of fluorene and fluorene-argon measurements, and the results are compared with data from previously published high-resolution frequency domain studies.

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**I. Introduction**

Recently, we have reported$^{1-3}$ on the use of Doppler-free picosecond spectroscopy to determine excited-state rotational constants and molecular structures for large molecules in their excited states. This approach is based on the phenomenon of purely rotational coherence. The theoretical foundation of purely rotational coherence and observations of its effects in jet-cooled molecules$^{4-8}$ and in a room-temperature vapor$^9$ have been the subjects of previously published works. A quantitative analysis of recurring transients in the polarization-analyzed fluorescence$^{1,3}$

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