Spin Relaxation Resonances due to the Spin-Axis Interaction in Dense Rubidium and Cesium Vapor

C. J. Erickson, D. Levron,* and W. Happer
Joseph Henry Laboratory, Physics Department, Princeton University, Princeton, New Jersey 08544

S. Kadlecek, B. Chann, L. W. Anderson, and T. G. Walker
Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706

(Received 5 July 2000)

Resonances in the magnetic decoupling curves for the spin relaxation of dense alkali-metal vapors prove that much of the relaxation is due to the spin-axis interaction in triplet dimers. Initial estimates of the spin-axis coupling coefficients for the dimers (likely accurate to a factor of 2) are $|\lambda|/h = 290$ MHz for Rb; 2500 MHz for Cs.

PACS numbers: 33.35.+r

Hot, dense alkali-metal vapors are used to polarize the nuclear spins of noble gases, especially ^{3}He and ^{129}Xe, by spin-exchange optical pumping [1]. Applications of these "hyperpolarized" noble gases in medical imaging [2] and fundamental physics [3] are of considerable current interest. Nevertheless, the basic physical limits to the efficiency of the spin-exchange process are still not fully understood. Under typical operating conditions of Rb-^{3}He spin exchange polarizers (saturated Rb vapor at 200 °C in 8 amagat of ^{3}He), about 45% of the Rb spin depolarization is due to Rb-Rb collisions [4]. Here we report conclusive experimental evidence that much of the spin relaxation in dense alkali-metal vapors comes from the spin-axis interaction in triplet dimers. Our measured spin-axis coupling strengths also impact the field of ultracold collisions, where the spin-axis interaction causes trap loss and affects the widths and positions of Feshbach resonances [5,6].

In 1959, Anderson *et al.* [7] showed that the dominant effect of binary collisions between alkali-metal atoms is the exchange of the electron spins. In 1974, Gupta *et al.* [8] showed that the spin angular momentum of the alkali-metal atoms was freely exchanged with the nuclear spin of the singlet dimers, for example, Rb_2 and Cs_2 (where nuclear quadrupole interactions cause some spin depolarization). In 1980, Bhaskar *et al.* [9] showed that Cs-Cs interactions destroy spin at about 1% of the spin-exchange rate. The rate coefficient for Cs-induced relaxation showed little dependence on buffer gas pressure or species. Relaxation mechanisms in singlet or triplet dimers were expected to depend strongly on pressure. Consequently, Bhaskar *et al.* [9] proposed that the relaxation was due to binary collisions between alkali-metal atoms. They pointed out that although there should be a spin-rotation interaction, $V_{\rm sr} = \gamma \mathbf{N} \cdot \mathbf{S}$ in the triplet dimers—similar to that postulated by Bernheim [10]—the coupling coefficient γ was probably too small to account for relaxation in binary collisions. Instead, they suggested that the source of the relaxation was a spin-axis interaction of the classic form [11]

$$V_{\rm sa} = \frac{2\lambda}{3} \mathbf{S} \cdot (3\boldsymbol{\zeta}\boldsymbol{\zeta} - \mathbf{1}) \cdot \mathbf{S}. \qquad (1)$$

Here $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ is the total electron spin of the colliding pair, and $\boldsymbol{\zeta}$ is a unit vector along the direction of the internuclear axis. The spin-axis coupling coefficient $\lambda = \lambda(R)$ arises from both the interaction energy of the electrons' magnetic dipole moments and the spin-orbit interaction in second order [12].

Because Knize's [13] measurements also showed little dependence of the Rb-induced relaxation on He or N_2 pressure, it came as a surprise when, in 1998, Kadlecek, Anderson, and Walker [14] discovered that the relaxation could be substantially suppressed by externally applied magnetic fields of a few thousand Gauss. If the interaction were due to pairs of alkali-metal atoms interacting on the triplet potential curve, this field dependence sets a lower limit on the correlation time of 40 ps, the inverse of the electron Larmor frequency at the decoupling field and a time much longer than the duration of a binary collision. Similar magnetic decoupling curves for K and Cs vapors were soon observed in our laboratories at Wisconsin and Princeton.

Although we still do not understand the relaxation at He or N_2 pressures of an atmosphere or more, recent low-pressure experiments leave no doubt that an important part of the spin relaxation in dense alkali-metal vapors comes from the spin-axis interaction (1), acting in triplet dimer molecules—even though the triplet dimer density is no more than 10^{-6} that of the monomers. The key experimental observation is the existence of resonances in the magnetic decoupling curves, resonances which are predicted from the spin-axis interaction (1), and which cannot be produced by the spin-rotation interaction or by spin-1/2 species such as trimer molecules.

A representative arrangement for measuring relaxation transients in Rb is shown at the top of Fig. 1. The alkali vapor and N_2 buffer gas were contained in 1 in. spherical

0031-9007/00/85(20)/4237(4)$15.00

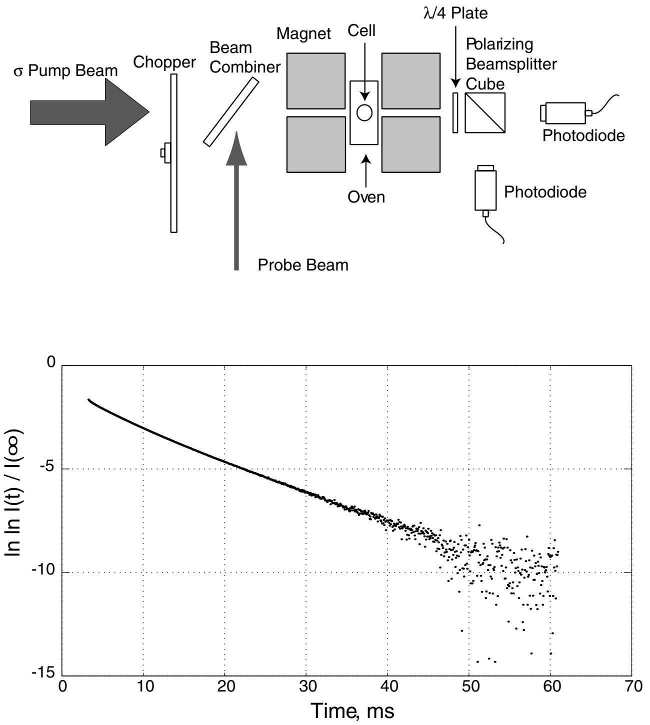

FIG. 1. Top: experimental apparatus for measuring the spin relaxation of Rb vapor. Bottom: representative transient decay curve obtained with the apparatus; at late times the transient decay is characterized by a single exponential time constant.

glass bulbs that were heated in an oven placed between the pole faces of a 10 kG electromagnet. We measured the number density of Rb atoms using Faraday rotation [15] of a tunable diode laser [16].

An intense pulse of 7947 Å circularly polarized pump laser radiation built up the spin polarization for a short (10 ms) interval. The pump laser was then blocked by the chopper wheel, and photodiodes monitored the transmission of a weak linearly polarized probe laser through the cell. The probe beam was resolved into its two circular components, giving positive and negative helicity signals $V_\pm(t)$ for sampling times t. The signal ratio $I(t) = V_+(t)/V_-(t)$ greatly suppressed probe-laser noise. The difference in the attenuation coefficients of the two circular components of the probe laser is proportional to the spin polarization P (for $P \ll 1$) of the vapor, so $\ln I(t) = a + bP(t)$, where $a = \ln I(\infty)$ and b are constants. Figure 1 shows a typical decay transient $\ln \ln I(t)/I(\infty)$. For early times, the decay is not exponential since the faster eigenmodes [17] of spin relaxation are still contributing to the polarization P. However, at late times there is a time interval, several e-foldings in length, over which $\ln \ln I(t)/I(\infty)$ is nearly a straight line with a slope $-\gamma$. Thus, when the polarization has decayed for a sufficiently long time, it is characterized by a single, exponential *late-time decay rate* γ.

The late-time decay rates of polarized Cs vapor in N_2 gas were measured as described previously [14], using Faraday rotation of linearly polarized light both to measure the Cs density and to monitor the spin polarization.

Representative measurements of γ in ^{87}Rb are shown in Fig. 2(a), where one can recognize three well-resolved resonances on the magnetic decoupling curve at magnetic fields of approximately 900, 1500, and 2100 G. Similar representative data for ^{133}Cs are shown in Fig. 3, where the theoretical curve has seven poorly resolved resonances, which nevertheless provide a good fit to the experimental data.

Also shown in Fig. 2(b) are representative energies of the spin sublevels of the triplet dimer molecules of ^{87}Rb for a value of the total nuclear spin quantum number $I = 2$. The resonances in the relaxation rate occur at the same magnetic fields as anticrossings in the energy level diagrams. The anticrossings are the result of the spin-axis interaction (1), acting in a total spin Hamiltonian

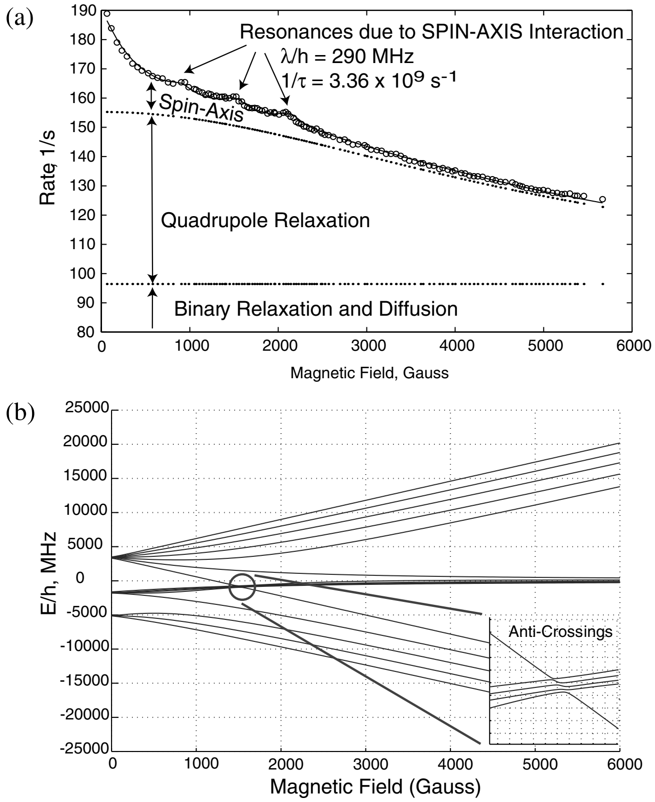

FIG. 2. (a) Late-time decay rate of ^{87}Rb versus magnetic field B. Resonant enhancements of the decay rate are observed at the fields $B_1 = 915$ G, $B_2 = 1526$ G, and $B_3 = 2136$ G, in agreement with the predicted values $B_I = A(2I + 1)/4g_S\mu_B$. The cell contained 0.061 amagat of N_2 gas. The cell temperature was 220 °C. The solid line is a theoretical fit assuming a field-independent contribution to γ of 97 $\sec^{-1}$ from binary collisions and diffusion to the cell walls, a field-dependent contribution from quadrupole interactions in singlet dimers, calculated as outlined in Ref. [8], and a contribution from a spin-axis interaction in triplet dimers, calculated according to Eq. (4). (b) Energy levels for a representative spin space with $I = 2$. The level anticrossings (inset) are responsible for the resonances in the magnetic decoupling curves.

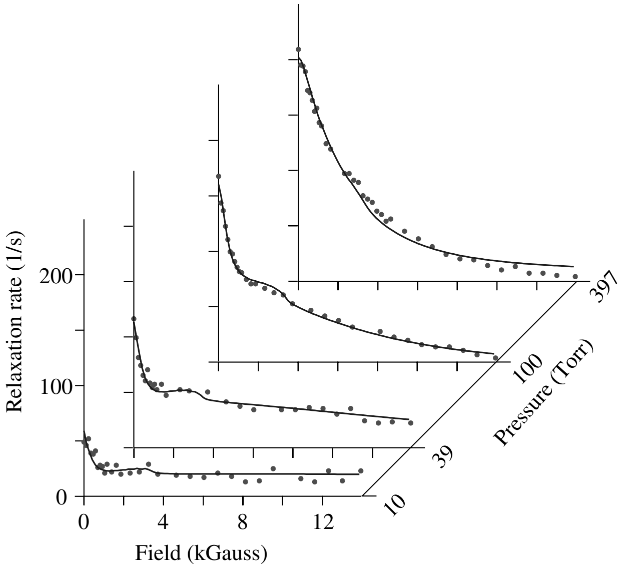

FIG. 3. Late-time field-dependent decay rate of ^{133}Cs versus magnetic field and pressure at 180 °C, $[\mathrm{Cs}] = 6.6 \times 10^{14}$ cm^{-3}. The cell temperature was 177 °C. The fits to the data use the reorientation model with negative λ.

for homonuclear triplet dimers of the form

$$H = \frac{A}{2}\mathbf{S}\cdot\mathbf{I} + g_s\mu_B B S_z - \frac{\lambda}{3}\mathbf{S}\cdot(3\mathbf{nn} - \mathbf{1})\cdot\mathbf{S}\,. \tag{2}$$

Here A is the magnetic-dipole hyperfine coupling coefficient for the free alkali atoms [$A(^{87}\mathrm{Rb})/h = 3\,417.4$ MHz and $A(^{133}\mathrm{Cs})/h = 2\,298.2$ MHz]. The operator for the total nuclear spin, $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ is the sum of the nuclear spin operators $\mathbf{I}_1$ and $\mathbf{I}_2$ for the two atoms. The operator $\mathbf{I}\cdot\mathbf{I}$ commutes with (2), and for homonuclear dimers its eigenvalues $I(I+1)$ can have $I = 0, 1, 2, \ldots, 2I_m$, where $I_m = I_1 = I_2$ is the nuclear spin quantum number of a monomer. The Hamiltonian (2) can therefore be diagonalized in a spin subspace I of dimension $3(2I+1)$ to find eigenfunctions $|i\rangle = |Ii\rangle$ and eigenvalues $E_i = E_{Ii}$. For $\lambda = 0$ there is a curious degeneracy in the spin subspace $I \neq 0$, with $2I + 1$ sublevels crossing at the magnetic field $B_I = A(2I+1)/4g_S\mu_B$. The last term in (2) is the spin-axis interaction (1), where we assume that the rotational angular momentum $\mathbf{N}$ of the dimers is large enough that we may treat it as a classical vector, pointing along the unit vector $\mathbf{n} = \mathbf{N}/N$, and make the replacement $(3\boldsymbol{\zeta\zeta} - \mathbf{1}) \to -(3\mathbf{nn} - \mathbf{1})/2$.

We estimate the relaxation caused by the interaction (2) with the following simple model. Let the total longitudinal spin operator of the triplet dimer be $G_z = S_z + I_z$. When triplet dimers are formed in dense alkali-metal vapors with low spin polarization, the spin density matrix of the dimers will be very nearly $\rho(0) = e^{\beta G_z}/Z$, where $\beta \approx 4P \ll 1$ is the spin-temperature parameter [7]. The partition function is very nearly $Z = 3(2I_m + 1)^2$. The spin of the dimer at the instant of formation is therefore $\langle G_{z0}\rangle = 2(I_m^2 + I_m + 1)\beta/3$, where we have neglected nonlinear terms in the small parameter β. The mean change in the density matrix by the time it breaks up again is $\Delta\rho = \langle U\rho(0)U^{-1}\rangle - \rho(0)$, where the time evolution operator is $U = e^{-iHt/\hbar}$, and the angle brackets $\langle\cdots\rangle$ denote an average over all directions of $\mathbf{n}$ and also an average over the probability, $e^{-t/\tau}dt/\tau$, that the dimer will break up in the time interval between t and $t + dt$. The collisional breakup rate of the dimers is $1/\tau$. The mean change in the dimer spin is therefore $\langle\Delta G_z\rangle = \mathrm{Tr}\{G_z\Delta\rho\} = -W\langle G_{z0}\rangle$, where the spin-destruction probability is

$$W = 2\sum_{ij}\frac{|\langle i|G_z|j\rangle|^2(\omega_{ij}\tau)^2}{(2I_m+1)^2[(2I_m+1)^2+3][1+(\omega_{ij}\tau)^2]}, \tag{3}$$

and the Bohr frequencies are $\omega_{ij} = (E_i - E_j)/\hbar$. An average over the directions of $\mathbf{n}$ is to be understood in (3). Almost all of the spin is carried by monomers of number density [Ak] (e.g., [Ak] = [Rb] or [Ak] = [Cs]), which have a spin density per unit volume $[\mathrm{Ak}]\beta(4I_m^2 + 4I_m + 3)/12$. The spin loss rate per unit volume from triplet dimers of number density $[\mathrm{Ak}_2]$ is $[\mathrm{Ak}_2]\langle\Delta G_z\rangle/\tau$, from which one obtains the relaxation equation $-(d/dt)\ln\beta = \gamma = \kappa[\mathrm{Ak}]$, where the rate coefficient is

$$\kappa = 2\left[\frac{(2I_m+1)^2+3}{(2I_m+1)^2+2}\right]\frac{W\mathcal{K}}{\tau}\,. \tag{4}$$

The chemical equilibrium coefficient of the triplet dimers is $\mathcal{K} = [\mathrm{Ak}_2]/[\mathrm{Ak}]^2$. We have used the theoretical triplet dimer potential curves of Krauss and Stevens [18] to estimate $\mathcal{K}(\mathrm{Rb}) = 330$ Å^3 and $\mathcal{K}(\mathrm{Cs}) = 650$ Å^3 at representative temperatures of 220 and 180 °C, respectively.

Nonvanishing values of λ lift the degeneracy at the field B_I and convert the level crossings into anticrossings, while making the corresponding matrix element $\langle i|G_z|j\rangle$ nonzero, as is illustrated in Fig. 2. It is these anticrossings of the energy levels that are responsible for the resonances, most clearly visible in Fig. 2. Remarkably, the spin-rotation interaction does not break the degeneracy, so the spin-axis interaction must be responsible for the relaxation resonances. Since there are $2I_m$ nonvanishing values of I for atoms with the nuclear spin quantum number I_m, we expect three resonances for ^{87}Rb with $I_m = 3/2$, as observed, and seven resonances, at fields between 600 and 3100 G for ^{133}Cs with $I_m = 7/2$, which fits well the observed field dependence shown in Fig. 3.

We fit the experimental data to theoretical curves which include a field-independent part due to diffusion to the cell walls and binary collisions, a field-dependent nuclear quadrupole relaxation in singlet dimers (negligible for Cs), and relaxation due to the spin-axis interaction in triplet dimers. We expect a small portion of the relaxation in triplet dimers to arise from the spin-rotation interaction, and we may estimate the magnitude of this relaxation mechanism by assuming that the spin-rotation interaction of Rb-Rb triplet dimers is the same as that of Rb-Kr, and that the spin-rotation interaction for Cs-Cs is the same as that for Rb-Xe, both of which are experimentally known from the work of Bouchiat *et al.* [19]. These estimates should be fairly reliable since the spin-orbit interaction that produces the spin-rotation coupling [1] varies only slightly from Rb to Kr or Cs to Xe. By using these estimates for $\gamma \mathbf{N} \cdot \mathbf{S}$, we find that the addition of the spin-rotation interaction causes a few percent change in the predicted relaxation rates.

In the model described above, the relaxation due to triplet dimers depends on two parameters: λ and the molecular lifetime τ, assuming that the theoretical values for $\mathcal{K}$ are accurate. The molecular lifetime should be inversely proportional to pressure, making it natural to introduce a cross section $\sigma = (\tau[\mathrm{N}_2]\overline{v})^{-1}$. Our Rb data is well described over the limited pressure range from 50 to 300 Torr by the values $|\lambda| = 290$ MHz and $\sigma = 290$ Å^2. The latter is somewhat larger than the typical 150 Å^2 breakup cross sections deduced from magnetic decoupling studies of Rb-Kr [19]. The sign of λ cannot be determined from the data.

Since there is little contribution to Cs relaxation from singlet molecules, relaxation from Cs-Cs triplet molecules can be observed over a wider range of pressures. Figure 3 shows a sampling of our spin-relaxation data for Cs as a function of magnetic field at a variety of N_2 pressures. In this case the data are well described by $\lambda = -2.9$ GHz, $\sigma = 98$ Å^2, and $\mathcal{K} = 350$ Å^3 or, assuming the opposite sign of λ, $\lambda = 3.4$ GHz, $\sigma = 82$ Å^2, and $\mathcal{K} = 307$ Å^3. The deduced values of $\mathcal{K}$ are about a factor of 2 smaller than predicted from the potential curves (which are believed to be fairly reliable). We have also fit the data with a model that allows for collisional reorientation of the triplet molecules without breakup, making the assumption that a spin-temperature distribution describes the dimer density matrix after reorientation. In this case τ in Eq. (3) is replaced by the coherence time τ_c, and $\overline{W} = W\tau/[\tau_c + (\tau - \tau_c)W]$ replaces W in Eq. (4). In this case we obtain $\lambda = -2.13$ GHz, $\sigma_c = 81$ Å^2, $\sigma = 42$ Å^2, and $\mathcal{K} = 584$ Å^3 or $\lambda = 2.71$ GHz, $\sigma_c = 93$ Å^2, $\sigma = 55$ Å^2, and $\mathcal{K} = 431$ Å^3. We emphasize that single values of λ and σ_c accurately represent the magnetic field dependences at nine pressures (not all shown in Fig. 3), covering nearly two decades in pressure.

Spin-axis coupling in Cs triplet dimers is also of current interest for studies of ultracold collisions [5] since it produces loss of spin-polarized atoms in magnetic traps, and affects the widths and positions of Feshbach resonances in Cs collisions [6]. The magnitude and sign of λ, as well as its dependence on interatomic separation R were predicted by Mies *et al.* [12]. Previous analysis [5] led to the conclusion that in order to agree with experiment the second-order spin orbit calculated by Mies *et al.* needed to be scaled by a factor of $S_C = 4.0 \pm 0.5$, recently updated to 3.2 ± 0.5 [6]. We find that, by averaging $\lambda(R)$ over the rovibrational levels of the triplet state using the Krauss and Stevens potentials [18], scaling factors of $S_C = 12$ for Rb and $S_C = 3.6$ for Cs are needed to reproduce our data.

In conclusion, the resonances observed in the magnetic decoupling curves of Rb, coupled with the observed pressure and field dependences of Cs, prove that a major contribution to the spin relaxation of hot, dense alkali-metal vapors is caused by the spin-axis interaction in triplet dimers. Knowing this key piece of the physics should help to unravel the still-puzzling independence of the relaxation rates on He and N_2 pressures of an atmosphere or more [14].

Support for this research came from NSF (Wisconsin and Princeton), and NIH (Princeton).

---

*Permanent address: Nuclear Research Center, Beer Sheva, Israel.

[1] M. A. Bouchiat, T. R. Carver, and C. M. Varnum, Phys. Rev. Lett. **5**, 373 (1960); T. G. Walker and W. Happer, Rev. Mod. Phys. **69**, 629 (1997).

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

[3] T. E. Chupp, R. J. Hoare, R. L. Walsworth, and Bo Wu, Phys. Rev. Lett. **72**, 2363 (1994).

[4] A. Ben-Amar Baranga, S. Appelt, M. V. Romalis, C. J. Erickson, A. R. Young, G. D. Cates, and W. Happer, Phys. Rev. Lett. **80**, 2801 (1998).

[5] P. Leo, E. Tiesinga, P. Julienne, D. Walter, S. Kadlecek, and T. Walker, Phys. Rev. Lett. **81**, 1389 (1998).

[6] P. Leo, C. Williams, and P. Julienne, Phys. Rev. Lett. **85**, 2721 (2000).

[7] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **116**, 87 (1959).

[8] R. Gupta, W. Happer, G. Moe, and W. Park, Phys. Rev. Lett. **32**, 574 (1974). Note that, in Eq. (7) of this paper, the numerical coefficient 3/40 should have been 3/160.

[9] N. D. Bhaskar, J. Pietras, J. Camparo, W. Happer, and J. Liran, Phys. Rev. Lett. **44**, 930 (1980).

[10] R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

[11] M. H. Hebb, Phys. Rev. **49**, 610 (1936); C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), p. 182.

[12] F. H. Mies, C. Williams, P. Julienne, and M. Krauss, J. Res. Natl. Inst. Stand. Technol. **101**, 521 (1996).

[13] R. Knize, Phys. Rev. A **40**, 6219 (1989).

[14] S. Kadlecek, L. W. Anderson, and T. G. Walker, Phys. Rev. Lett. **80**, 5512 (1998).

[15] Z. Wu, M. Kitano, W. Happer, M. Hou, and J. Daniels, Appl. Opt. **25**, 4483 (1986).

[16] K. B. MacAdam, A. Steinbach, and C. Wieman, Am. J. Phys. **60**, 1098 (1992).

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

[18] M. Krauss and W. J. Stevens, J. Chem. Phys. **93**, 4236 (1990).

[19] M. A. Bouchiat, J. Brossel, and L. C. Pottier, J. Chem. Phys. **56**, 3703 (1972).