Collisional transfer of electronic state coherence

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The role of collision-induced transfer of electronic state coherence on the spectral response of an atomic vapor is investigated. It is shown that such collisional effects can lead to the appearance of narrow resonances in the nonlinear spectroscopy of three-level systems. Collisional transfer between different multipoles of electronic state coherence is shown to lead to a breakdown of several percent in Becquerel's relation between the Faraday rotation and dispersion of a vapor. All calculations are carried out in the impact limit of pressure broadening theory. Particular emphasis is given to the order in which the various averages over the velocity distributions of both the active atoms and perturbers must be performed. In particular, for the effects described herein, the various collisional transfer rates vanish when averaged over the active atom velocity distribution. It is essential, therefore, to obtain the final lineshape formulas, including velocity-dependent collisional transfer rates, before carrying out the average over the active atom velocity distribution. The experimental observation of these spectral features would provide direct evidence for the existence of these collisional transfer processes.

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I. INTRODUCTION

It is well known that collisional processes can significantly modify the spectral response of atomic vapors. The collisional broadening of spectral profiles and collision-induced mixing of magnetic state sublevels have been studied extensively. On the other hand, investigations of collision-induced transfer of electronic state coherence (CITEC) have received only limited attention [1–4]. In this paper, several aspects related to the collision-induced transfer of electronic state coherence are examined. In particular, it is shown that CITEC can lead to new features in the spectral response of atomic vapors. The appearance of such features would, in turn, provide evidence for such collisional processes.

It is not surprising that CITEC has not been studied as extensively as other collisional effects. Nature seems to conspire to guarantee that the transfer rates associated with CITEC are either small or identically zero. Consider, for example, the level scheme shown in Fig. 1. A circularly polarized laser field propagating in the $\hat{\mathbf{z}}$ direction drives an atomic transition between a $j=0$ ground state and a $j=1$ excited state. If the field is σ^- polarized, it creates an electronic state coherence between the ground state and the $m=-1$ sublevel of the excited state. Is it possible for collisions to transfer this coherence to a coherence between the ground state and the $m=1$ sublevel of the excited state?

At first glance, one might think that such transfer rates must vanish owing to random phases that accompany the collisional transfer of electronic state coherence. Although there *is* a phase change associated with the collisional transfer, it is not sufficient, on average, to totally destroy the electronic dipole phase that has been created by the laser field [5]. As a consequence, it would seem that the collisional transfer can occur. At this stage, however, one points out that, owing to symmetry considerations [5,6], the collisional transfer rate for the process indicted in Fig. 1 vanishes when averaged over all possible collision orientations, provided that the perturber velocity distribution is axially symmetric with respect to the quantization axis (taken along the $\hat{\mathbf{z}}$ axis).

Although the average transfer rate vanishes, there can *still* be modifications of spectral profiles that result from the coherence transfer. To illustrate this point, let us consider the atomic level scheme shown in Fig. 2. Levels 1, 2, and 3 have angular momentum $j=0$, 1, and 0, respectively. Density-matrix elements are written as $\rho_{j_i m;j_k m'} \equiv \rho_{mm'}(i,k)$. The atom is prepared in level 1 and is subjected to two counterpropagating laser fields. The first field is σ^- polarized and is detuned from the j_1 to j_2 transition by a frequency that is greater than the Doppler width associated with that transition, but smaller than the inverse duration of a collision. The second field is also σ^- polarized and the population of level 3 is measured as a function of the second laser field's frequency. Suppose now that a resonance appears when the sum of the incident laser frequencies is equal to the frequency spacing between levels 1 and 3. Such a resonance can result only from the type of coherence transfer process described above. In other words, the first field creates the coher-

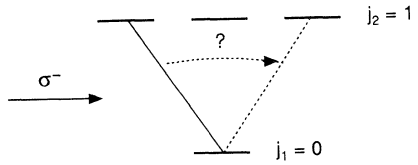

FIG. 1. σ-polarized radiation creates a coherence between the ground state and the $m=-1$ sublevel of the excited state. The question under investigation is whether or not collisions can result in a transfer that leads to a coherence between the ground state and the $m=1$ sublevel of the excited state.

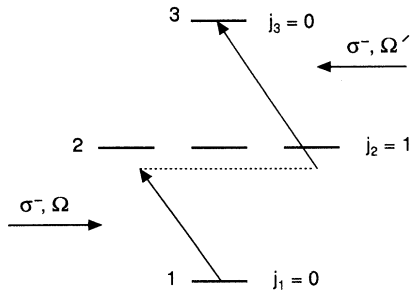

FIG. 2. A three-level scheme in which the field having frequency Ω drives the $j_1=0$ to $j_2=1$, $m_2=-1$ transition and the field having frequency Ω' probes the $j_2=1$, $m_2=1$ to $j_3=0$ transition. As a result of the collisional transfer of electronic state coherence, a resonance appears when $(\Omega+\Omega')=\omega_{31}$ if the upper state population is measured as a function of Ω' for fixed Ω. The detuning $(\Omega-\omega_{21})$ is assumed to be large compared with the Doppler width and collisional width associated with the $j_1=0$ to $j_2=1$, $m_2=-1$ transition.

ence $\rho_{0,-1}(1,2)$. Collisions must transfer this coherence to produce $\rho_{01}(1,2)$ so that the second field can complete the two-photon excitation of level 3. Does such a resonance occur?

As shown in detail below, the two-photon resonance appears as a result of the collisional coherence transfer. In this case, the contribution to the line shape depends on the *absolute square* of the coherence transfer rate $\Gamma_{tr}(\mathbf{v})$, averaged over the active atoms' velocity distribution $W(\mathbf{v})$. The rate $\Gamma_{tr}(\mathbf{v})$ contains an average over the perturber velocity distribution for an active atom *moving with velocity* $\mathbf{v}$ (for details, see Sec. II). For active atoms having $\mathbf{v}$ along the quantization axis, $\Gamma_{tr}(\mathbf{v})$ vanishes, but for active atoms moving in other directions, $\Gamma_{tr}(\mathbf{v})$ is nonzero. As a result, the average of $|\Gamma_{tr}(\mathbf{v})|^2$ over $W(\mathbf{v})$ leads to a nonvanishing contribution to the line shape. This is the first class of CITEC processes considered in this paper, those for which CITEC contributes to the line profile despite the fact that $\langle\Gamma_{tr}(\mathbf{v})\rangle$, the average of $\Gamma_{tr}(\mathbf{v})$ over $W(\mathbf{v})$ $\langle\Gamma_{tr}(\mathbf{v})\rangle$, vanishes. The limited experimental observation of atomic or molecular dipole coherence transfer has been in systems for which $\langle\Gamma_{tr}(\mathbf{v})\rangle\neq 0$ [2–4].

A second class of CITEC reactions has been studied, motivated in large part by the recent work of Kristensen, van Eijkelenborg, and Woerdman [7]. Working with Rb active atoms in a high-density ($\sim 10^{20}$ cm^{-3}) Xe buffer gas, these authors observed a deviation from Becquerel's relation between the Faraday rotation and dispersion in an atomic vapor. The deviations were attributed to effects related to the breakdown of the binary collision approximation. It is shown below that, as a result of CITEC, a breakdown of Becquerel's relation also occurs at perturber pressures where the binary collision approximation is valid. It is unlikely that the CITEC reactions to be discussed in this paper are responsible for the observations of Kristensen, van Eijkelenborg, and Woerdman [7], but they can, nevertheless, lead to experimentally observable effects.

The modification of Becquerel's law is seen most easily if one expresses density-matrix elements in an irreducible tensor basis. The density-matrix elements are then identified by multipole order k and component q $[-(2k+1)\leq q\leq(2k+1)]$. A breakdown of Becquerel's relation occurs if collisions result in a transfer of electronic state coherence between different multipoles (for details, see Sec. IV). In contrast to the first class of CITEC processes, this effect depends linearly on the multipole transfer rate to lowest order (there is always a small, but nonvanishing, violation of Becquerel's law resulting from contributions that are second order in the transfer rates). Since the multipole transfer rates vanish when averaged over an isotropic active-atom velocity distribution and to first order in the external fields, the active-atom velocity distribution *is* isotropic, one might think that any corrections to Becquerel's law that vary linearly with the transfer rates would vanish. This conclusion is not valid, however, since the linear atomic response depends on the dipole coherence density, which is not an isotropic function of active-atom velocity owing to the fact that the Doppler shift in an active atom's rest frame is an anisotropic function of its velocity. As a consequence, multipole transfer of atomic state coherence can lead to corrections to Becquerel's law. Although multipole transfer *within* a state of given angular momentum has been studied both theoretically and experimentally [8–11], there does not appear to be similar studies of multipole transfer of electronic state coherence.

This paper is organized as follows. A qualitative discussion of the problem and the approximations of the theory are given in Sec. II. In Sec. III the line shape corresponding to the configuration shown in Fig. 2 is calculated and in Sec. IV the role of multipole transfer in modifying Becquerel's relation is examined. A summary and discussion of the results is given in Sec. V. Details of the collision models and derivation of the various collisional transfer rates are presented in the Appendixes.

II. QUALITATIVE DISCUSSION AND APPROXIMATIONS

The physical system consists of "active" atoms in a vapor cell which interact with one or more external laser fields. The active atoms also undergo collisions with perturber atoms (which are unaffected by the laser fields). The incident laser fields all propagate along the same axis, which is chosen as the quantization axis for the system. It is also possible that a static magnetic field is applied in the direction of the quantization axis.

Calculations are carried out to lowest nonvanishing order in the applied radiation fields. Collisions are treated in the impact approximation, requiring that

$$\Gamma\tau_c \ll 1\ ,\quad |\Delta|\tau_c \ll 1\ ,\quad ku\tau_c \ll 1\ ,\quad \gamma\tau_c \ll 1\ ,\quad \delta\omega\tau_c \ll 1\ , \tag{1}$$

where τ_c is the collision duration, Γ the collision rate, Δ the atom-field detuning, ku the Doppler width (k is the laser-field propagation constant and u the most probable active atom speed), γ the atomic decay rate, and $\delta\omega$ the frequency spacing between sublevels within a state of

given electronic angular momentum j (including any Zeeman splitting of these levels). On the other hand, it is assumed that

$$\omega\tau_c \gg 1 , \quad \omega_{\rm FS}\tau_c \gg 1 , \tag{2}$$

where ω is the optical frequency and $\omega_{\rm FS}$ is a frequency spacing between fine-structure levels within a given electronic state. In other words, collisions can mix hyperfine levels and magnetic sublevels within a state of given j, but do not mix states of different j.

In the impact approximation, collisions result in a time rate of change of density matrix elements given by

$$\dot{\rho}_{mm'}(j_1,j_2;\mathbf{v}) = -\Gamma^{nn'}_{mm'}(j_1,j_2;\mathbf{v})\rho_{nn'}(j_1,j_2;\mathbf{v}) , \tag{3}$$

where $\mathbf{v}$ is the active atom velocity and $\Gamma^{nn'}_{mm'}(j_1,j_2;\mathbf{v})$ is the (complex) collisional decay or transfer rate. In Eq. (3) and all subsequent equations, a summation convention is adopted in which all repeated indices on the right-hand side of an equation are summed over unless the indices also appear on the left-hand side of the equation. Explicit expressions for the transfer rates are given in the Appendixes, derived under the assumption that the colliding atoms follow straight-line paths. All effects related to collision-induced changes in atomic velocity are neglected in this paper.

Equation (3) may also be written in an irreducible tensor basis as

$$\dot{\rho}^k_q(j_1,j_2;\mathbf{v}) = -\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})\rho^{k'}_{q'}(j_1,j_2;\mathbf{v}) , \tag{4}$$

where

$$\rho^k_q(j_1,j_2;\mathbf{v}) = (-1)^{j_2-m'}\langle j_1 m, j_2 - m' | kq \rangle \times \rho_{mm'}(j_1,j_2;\mathbf{v}) \tag{5}$$

and $\langle j_1 m, j_2 m' | kq \rangle$ is a Clebsch-Gordon coefficient. In an irreducible tensor basis, the $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$ possess some simple symmetry properties [6,8–11].

It is important to note that the $\Gamma(\mathbf{v})$'s have already been averaged over the perturber velocity distribution, on the assumption that each time an active atom undergoes a collision, it does so with a reservoir of perturber atoms that has been affected negligibly by all previous collisions. The collision rates still depend on the active-atom velocity since active atoms having different velocities "see" *different* perturber velocity distributions in their rest frames. The larger the ratio of perturber to active atom mass, the more pronounced the dependence of $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$ on $\mathbf{v}$.

For $\mathbf{v}=0$, the perturber velocity distribution is isotropic and one finds [6]

$$\Gamma^{kk'}_{qq'}(j_1,j_2;0) = \Gamma^k(j_1,j_2;0)\delta_{qq'}\delta_{kk'} . \tag{6}$$

For atoms moving along the quantization axis, the axial symmetry of the perturber velocity distribution seen in the atoms' rest frame leads to the relationship [8]

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v}=v\hat{\mathbf{z}}) = \Gamma^{kk'}_{q}(j_1,j_2;\mathbf{v})\delta_{qq'} ; \tag{7}$$

that is, different multipoles can be coupled, but the q component, which is related to the difference in magnetic quantum numbers of states j_1 and j_2, cannot change for a perturber velocity distribution that is axially symmetric with respect to the quantization axis.

As a simplification, the rates appearing in Eq. (4) are sometimes preaveraged over the active-atom velocity distribution $W(\mathbf{v})$ to obtain [5,9–11]

$$\dot{\rho}^k_q(j_1,j_2;\mathbf{v}) = -\Gamma^{kk'}_{qq'}(j_1,j_2)\rho^{k'}_{q'}(j_1,j_2;\mathbf{v}) , \tag{8}$$

where

$$\Gamma^{kk'}_{qq'}(j_1,j_2) = \langle \Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v}) \rangle = \int W(\mathbf{v})\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})d\mathbf{v} . \tag{9}$$

For an isotropic active-atom velocity distribution

$$\Gamma^{kk'}_{qq'}(j_1,j_2) = \Gamma^k(j_1,j_2)\delta_{qq'}\delta_{kk'} , \tag{10}$$

while, for an active-atom distribution that is axially symmetric with respect to the quantization axis,

$$\Gamma^{kk'}_{qq'}(j_1,j_2) = \Gamma^{kk'}_{q}(j_1,j_2)\delta_{qq'} . \tag{11}$$

For many instances, Eq. (8) can be used without introducing significant error. Consider, however, a situation in which $\Gamma^{kk'}_{qq'}(j_1,j_2) = \langle \Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v}) \rangle = 0$, but one for which the final expression for the spectral line feature under investigation depends on $\langle |\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})|^2 \rangle \neq 0$. Use of Eq. (8) would then lead to a null result, whereas the actual spectral feature does not vanish. For the atom-field configurations to be discussed in Secs. III and IV, $\Gamma^{kk'}_{qq'}(j_1,j_2)=0$ for $k\neq k'$ or $q\neq q'$. If Eq. (8) rather than Eq. (4) were used to calculate the signals, none of the spectral features to be derived would emerge from the calculations. It is essential to use Eq. (4) and defer the average over the active-atom velocity distribution until the end of the calculation.

It may be worthwhile to point out that there can be a collisional transfer of electronic state coherence even if $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v}) = \Gamma^k(j_1,j_2;\mathbf{v})\delta_{qq'}\delta_{kk'}$. From Eqs. (3)–(5), it follows that, in the m basis, the corresponding transfer rates would be

$$\Gamma^{nn'}_{mm'}(j_1,j_2;\mathbf{v}) = (-1)^{m'-n'}\langle j_1 m, j_2 - m' | kq \rangle \times \langle j_1 n, j_2 - n' | kq \rangle \Gamma^k(j_1,j_2;\mathbf{v}) . \tag{12}$$

Coherence transfer is possible if $(m'-m)=(n'-n)$. One can then distinguish coherence transfer processes that are diagonal in k and q [Eq. (12)] from those that are nondiagonal in k or q (or both). Experimentally [2–4], coherence transfer diagonal in k and q has been observed. The coherence transfer processes to be described in secs. II and IV are nondiagonal in k and/or q.

III. COHERENCE TRANSFER IN NONLINEAR SPECTROSCOPY

I first consider the atomic level scheme in Fig. 2, since it is conceptually the easiest to illustrate the coherence transfer process. Variations on this level scheme which are more practical from an experimental viewpoint are discussed at the end of this section. A σ^--polarized laser

field drives the $j_1=0$ to $j_2=1$, $m_2=-1$ transition and a counterpropagating σ^--polarized laser field probes the $j_2=1$, $m_2=1$ to $j_3=0$ transition. The transition frequencies differ sufficiently to ensure that each field drives only a single transition. The fields are detuned from their respective transition frequencies by an amount that is larger than the Doppler widths associated with the transitions, but the sum of the two laser frequencies is close to that of the two-photon frequency between levels 1 and 3. The first field's frequency is held fixed and the upper state population ρ_{33} is probed as a function of the second field's frequency.

In the absence of collisions there is no excitation of level 3. Collisions lead to excitation of level 3 via two distinct (but interconnected) processes. First, collisions transfer coherence from $\rho_{0,-1}(1,2)$ to $\rho_{0,1}(1,2)$, which allows the second field to complete the two-photon transition to level 3. There is a competing process in which the first field (aided by collisions) creates a population in the $m=-1$ sublevel of state 2; collisions transfer this population to the $m=1$ sublevel and the second field completes the transition to level 3. The first process can be referred to as a two-quantum (TQ) contribution and the second a stepwise (SW) contribution to the final-state probability ρ_{33} [12]. The calculation is conveniently carried out using density-matrix elements in the m basis. In perturbation theory, the density-matrix chains responsible for the TQ and SW processes are shown in Fig. 3.

Let us first concentrate on the TQ chain since it involves the coherence transfer. In the first step of the perturbation chain, one must calculate $\rho_{0,-1}(1,2;\mathbf{v})$, which, in the rotating-wave or resonance approximation, evolves as [12,13]

$$\dot{\rho}_{0,-1}(1,2;\mathbf{v})=-[(\gamma_2/2)-i\omega]\rho_{0,-1}(1,2;\mathbf{v}) -\Gamma^{0,m}_{0,-1}(1,2;\mathbf{v})\rho_{0,m}(1,2;\mathbf{v}) -i\chi^* W(\mathbf{v})\exp[-i(kZ-\Omega t)] , \quad (13)$$

where γ_2 is the decay rate of state 2, $\omega=\omega_{21}$ is the 2 to 1 transition frequency,

$$\chi=\not{\mu}E/2\hbar \quad (14)$$

is the Rabi frequency, $\not{\mu}$ is the dipole moment matrix element between states $\langle j_2,-1|$ and $|j_1,0\rangle$, and E, Ω, and k are the amplitude, frequency, and propagation constant of the field propagating in the $\hat{\mathbf{z}}$ direction. The time derivative in Eq. (13) is a total time derivative $=\partial/\partial t+\mathbf{v}\cdot\nabla$. It turns out that the off-diagonal $\Gamma^{0,m}_{0,-1}(1,2;\mathbf{v})$'s are small compared to the diagonal ones. Thus, to a good approximation, Eq. (13) can be solved to yield

$$\rho_{0,-1}(1,2;\mathbf{v})=-[\chi^* W(\mathbf{v})/\mu_1(\mathbf{v})]\exp[-i(kZ-\omega t)] , \quad (15)$$

where

$$\mu_1(\mathbf{v})=(\gamma_2/2)+\Gamma^{0,-1}_{0,-1}(1,2;\mathbf{v})+i(\Delta-kv_z) \quad (16)$$

and

$$\Delta=\Omega-\omega . \quad (17)$$

The next step is to calculate the collisional transfer of this electronic coherence. The density-matrix element $\rho_{0,1}(1,2;\mathbf{v})$ evolves as

$$\dot{\rho}_{0,1}(1,2;\mathbf{v})=-[(\gamma_2/2)-i\omega]\rho_{0,-1}(1,2;\mathbf{v}) -\Gamma^{0,m}_{0,1}(1,2;\mathbf{v})\rho_{0,m}(1,2;\mathbf{v}) . \quad (18)$$

Using the fact that the nondiagonal Γ's are small relative to the diagonal ones and the fact that $\Gamma^{0,1}_{0,1}(1,2;\mathbf{v})=\Gamma^{0,-1}_{0,-1}(1,2;\mathbf{v})$, one finds

$$\rho_{0,1}(1,2;\mathbf{v})=-[\Gamma^{0,-1}_{0,1}(1,2;\mathbf{v})/\mu_1(\mathbf{v})]\rho_{0,-1}(1,2;\mathbf{v}) . \quad (19)$$

The next step is to evaluate $\rho_{0,0}(1,3;\mathbf{v})$, which evolves as

$$\dot{\rho}_{0,0}(1,3;\mathbf{v})=-[(\gamma_3/2)+i(\omega+\omega')]\rho_{0,0}(1,3;\mathbf{v})-\Gamma^{00}_{00}(1,3;\mathbf{v})\rho_{0,0}(1,3;\mathbf{v}) -i(\chi')^*\exp[i(k'Z+\Omega' t)]\rho_{0,1}(1,2;\mathbf{v})+i\chi^*\exp[-i(kZ-\Omega t)]\rho_{-1,0}(2,3;\mathbf{v}) , \quad (20)$$

where γ_3 is the decay rate of state 3, $\omega'=\omega_{32}$ is the 3 to 2 transition frequency,

$$\chi'=\not{\mu}'E'/2\hbar , \quad (21)$$

$\not{\mu}'$ is the dipole moment matrix element between states $\langle j_3,0|$ and $|j_3,1\rangle$, and E', Ω', and k' are the amplitude, frequency, and propagation constant of the field propagating in the $-\hat{\mathbf{z}}$ direction. Note that the last term in Eq. (20) does not contribute to this order in perturbation theory. Equation (20) can be solved to yield

$$\rho_{0,0}(1,3;\mathbf{v})=-i[(\chi')^*/\mu_{13}(\mathbf{v})] \times\exp[i(k'Z+\Omega' t)]\rho_{0,1}(1,2;\mathbf{v}) , \quad (22)$$

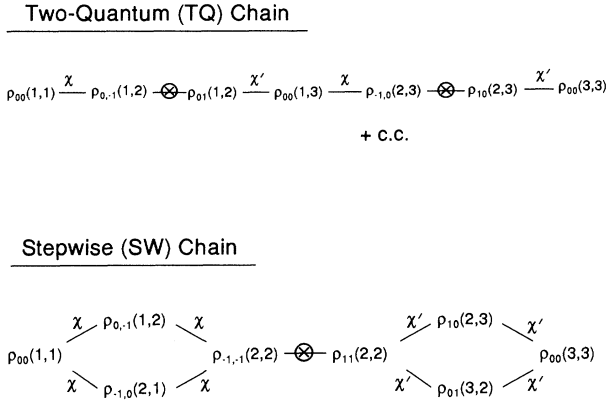

FIG. 3. In lowest-order perturbation theory, these are the two chains that lead to the excitation of level 3 in Fig. 2. The cross indicates a collisional interaction.

where

$$\mu_{13}(\mathbf{v})=(\gamma_3/2)+\Gamma_{00}^{00}(1,3;\mathbf{v})+i[(\Delta+\Delta'-(k-k')v_z] \tag{23}$$

and

$$\Delta'=\Omega'-\omega' . \tag{24}$$

The remainder of the calculation proceeds in a similar fashion and one arrives finally at a two-quantum contribution to $\rho_{33}(\mathbf{v})\equiv\rho_{00}(3,3;\mathbf{v})$ given by

$$\begin{aligned}\rho_{33}^{\mathrm{TQ}}(\mathbf{v})&=|\chi\chi'|^2W(\mathbf{v})\Gamma_{0,1}^{0,-1}(1,2;\mathbf{v})\\&\times[\Gamma_{0,1}^{0,-1}(3,2;\mathbf{v})]^*/\{\gamma_3[\mu_1(\mathbf{v})]^2\mu_{13}(\mathbf{v})[\mu_2(\mathbf{v})]^2\}\\&+\text{c.c.} ,\end{aligned} \tag{25}$$

where

$$\mu_2(\mathbf{v})=(\gamma_3+\gamma_2)/2+\Gamma_{-10}^{-10}(2,3;\mathbf{v})+i(\Delta'+k'v_z) \tag{26}$$

and the relationship $\Gamma_{1,0}^{-1,0}(2,3;\mathbf{v})=[\Gamma_{0,1}^{0,-1}(3,2;\mathbf{v})]^*$ has been used. An analogous calculation for the stepwise contribution yields

$$\begin{aligned}\rho_{33}^{\mathrm{SW}}(\mathbf{v})&=4|\chi\chi'|^2W(\mathbf{v})G(\mathbf{v})\Gamma_{12}(\mathbf{v})\\&\times\Gamma_{23}(\mathbf{v})/[\gamma_2\gamma_3|\mu_1(\mathbf{v})|^2|\mu_2(\mathbf{v})|^2] ,\end{aligned} \tag{27}$$

where

$$\begin{aligned}\Gamma_{12}(\mathbf{v})&=(\gamma_2/2)+\mathrm{Re}[\Gamma_{01}^{01}(1,2;\mathbf{v})] ,\\\Gamma_{23}(\mathbf{v})&=(\gamma_2+\gamma_3)/2+\mathrm{Re}[\Gamma_{10}^{10}(2,3;\mathbf{v})] ,\end{aligned} \tag{28}$$

and $G(\mathbf{v})$ is a factor that gives the fraction of population that is transferred from the $m=-1$ to the $m=1$ sublevel by collisions. Note that the TQ contribution arises solely from a collision-induced transfer of electronic state coherence. Moreover, since both $\Gamma_{0,1}^{0,-1}(1,2;\mathbf{v})$ and $\Gamma_{0,1}^{0,-1}(3,2;\mathbf{v})$ are proportional to the spherical harmonic $Y_2^2(\theta_v,\phi_v)$, the TQ contribution would have vanished had we used the average value for these collision rates in the equations for $\dot{\rho}_{mm'}(j_1,j_2)$. The TQ contribution depends on a bilinear product of these rates which does not vanish when averaged over the spherical angles θ_v and ϕ_v of the velocity $\mathbf{v}$ relative to the quantization axis.

Equations (25)–(27) are valid for any ratios of collision rates and detunings to Doppler width. For the limiting case of interest in which $|\Delta|\gg ku$, $\mathrm{Re}[\Gamma_{01}^{01}(1,2;\mathbf{v})]$; $|\Delta'|\gg k'u$, $\mathrm{Re}[\Gamma_{10}^{10}(2,3;\mathbf{v})]$; and $|k-k'|u\ll\mathrm{Re}[\Gamma_{00}^{00}(1,3)]$ the equations simplify considerably. An additional simplification is possible since the *diagonal* collision rates depend only slightly on the direction of $\mathbf{v}$ (see Appendix B). One can then replace $\Gamma_{12}(\mathbf{v})$ by $\Gamma_{12}(u)=\langle\Gamma_{12}(\mathbf{v})\rangle$ and $\Gamma_{23}(\mathbf{v})$ by $\Gamma_{23}(u)=\langle\Gamma_{23}(\mathbf{v})\rangle$ to reduce Eqs. (25) and (27) to

$$\rho_{33}^{\mathrm{TQ}}(\mathbf{v})=|\chi\chi'|^2\langle\Gamma_{0,1}^{0,-1}(1,2;\mathbf{v})[\Gamma_{0,1}^{0,-1}(3,2;\mathbf{v})]^*\rangle/[\gamma_3\Delta^2(\Delta')^2\mu_{13}]+\text{c.c.} , \tag{29}$$

$$\rho_{33}^{\mathrm{SW}}(\mathbf{v})=4|\chi\chi'|^2\langle G(\mathbf{v})\rangle\Gamma_{12}(u)\Gamma_{23}(u)/[\gamma_2\gamma_3\Delta^2(\Delta')^2] , \tag{30}$$

$$\mu_{13}=(\gamma_3/2)+i(\Delta+\Delta')+\Gamma_{00}^{00}(1,3;\mathbf{v}) \tag{31}$$

and the average is over $W(\mathbf{v})$.

In the region where $\Delta\simeq-\Delta'$, the TQ contribution exhibits a resonant structure with width of order $\Gamma_{13}(u)=(\gamma_3/2)+\mathrm{Re}\langle[\Gamma_{00}^{00}(1,3;\mathbf{v})]\rangle$, while the SW contribution provides a nearly constant background. The ratio r of the TQ to SW contribution is of order

$$\begin{aligned}r=\rho_{33}^{\mathrm{TQ}}/\rho_{33}^{\mathrm{SW}}&\sim|\langle\Gamma_{0,1}^{0,-1}(1,2;\mathbf{v})[\Gamma_{0,1}^{0,-1}(3,2;\mathbf{v})]^*\rangle|\\&\times\gamma_2/[2\langle G(\mathbf{v})\rangle\Gamma_{12}(u)\Gamma_{23}(u)\Gamma_{13}(u)] .\end{aligned} \tag{32}$$

The actual value of the ratio is model dependent, but it is possible to estimate its value using the calculations of Appendixes A and B. For a dipole-dipole collisional interaction and for perturber pressures sufficiently high such that the diagonal collisional decay rates are greater than the spontaneous decay rates, the ratio r is estimated as

$$r=c_1[\gamma_2/\Gamma_{13}(u)]\{\lambda[(m_p/m)^{1/2}]\}^2 , \tag{33}$$

where m and m_p are the active atom and perturber masses, respectively, and $\lambda(x)$ is a function plotted in Fig. 4 as a function of $x^2=(m_p/m)$. The coefficient c_1 is model dependent and ranges from a value of 0.0042 if the collision-induced phase shifts of the various levels have opposite signs to 0.4 if there is a fortuitous cancellation of phase shifts having the same sign and comparable magnitudes. In deriving Eq. (33), I set $\langle G(\mathbf{v})\rangle=\frac{1}{3}$ since, in the limit of collision rates larger than spontaneous decay

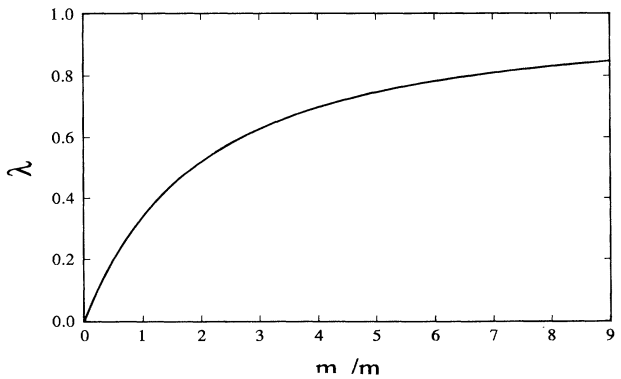

FIG. 4. The parameter λ as a function of the ratio of the perturber to the active-atom mass ratio. The collisional processes considered in this work are favored by higher values of λ.

rates, collisions totally redistribute the population in the $j_2=1$ level. In a spherical basis, both $\Gamma^{0,-1}_{0,1}(1,2;\mathbf{v})$ and $\Gamma^{0,-1}_{0,1}(3,2;\mathbf{v})$ appearing in Eq. (32) represent terms that are nondiagonal in the index q. As noted in Sec. II, the magnitude of these elements depends on the degree of anisotropy of the perturber velocity distribution seen in the active atom's rest frame. The degree of anisotropy is larger for larger ratios of m_p to m. This fact is reflected in the dependence of the ratio r on the function $\lambda[(m_p/m)^{1/2}]$.

Since $\gamma_2/\Gamma_{13}(u)\ll 1$, the ratio of the TQ to SW term is small. This condition can be remedied if we can find a system in which the density-matrix element $\rho_{mm'}(1,3)$ is unaffected by collisions and decays at a rate much slower than γ_2. Such systems are readily available. If instead of the three-level scheme of Fig. 2 we use a Λ scheme in which levels 1 and 3 are now different ground-state sublevels of an alkali-metal atom, the collisional decay rate associated with density-matrix element $\rho_{mm'}(1,3)$ is small compared with the excited-state decay rate γ_2. The ratio of the TQ to SW contribution will then scale as (γ_2/γ_t), where γ_t is the inverse time that the atom spends in the interaction volume. Since values of $(\gamma_2/\gamma_t)\geq 1000$ can be realized, the TQ contribution can dominate the spectral response. As such, the signal can be a direct measure of the existence of CITEC.

Consider, for example, the level scheme of Fig. 5, which corresponds to an alkali-metal atom. Only the $j_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$ transition is shown since all nondiagonal decay rates vanish for a $j_1=\frac{1}{2}$ to $j_2=\frac{1}{2}$ transition. The cross section for m-changing collisions in the ground state is negligibly small, since the ground state is an S state. To approximate a "three-level" atom, it is assumed that a static magnetic field has been applied along the z axis and that the resulting Zeeman splitting is large compared with the Doppler width associated with the j_1 to j_2 transition and with the hyperfine splitting of the levels, but small compared with the inverse collision duration.

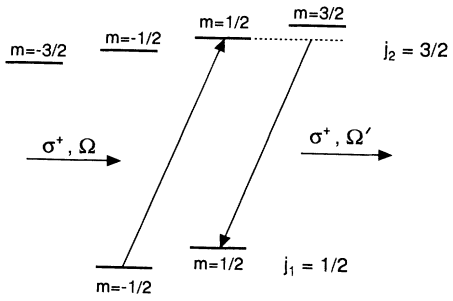

FIG. 5. An atomic level scheme, appropriate to an alkali-metal atom in an external magnetic field, which can be used as a "three-level" system. The magnetic field splitting is larger than the Doppler width, such that each of the incident fields can be assumed to drive a single transition. The field having frequency Ω drives the $j_1=\frac{1}{2}$, $m_2=-\frac{1}{2}$ to $j_2=\frac{3}{2}$, $m_2=\frac{1}{2}$ transition and the field having frequency Ω' probes the $j_1=\frac{1}{2}$, $m_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$, $m_2=\frac{3}{2}$ transition. The atom is prepared in the $m_1=-\frac{1}{2}$ sublevel and the population of the $m_1=\frac{1}{2}$ sublevel is monitored as a function of Ω' for fixed Ω.

Two copropagating, σ^+-polarized fields are used. The one having frequency Ω is nearly resonant with the $j_1(m=-\frac{1}{2})$ to $j_2(m=\frac{1}{2})$ transition frequency. The second field's frequency Ω' is chosen such that the difference $(\Omega-\Omega')$ is nearly resonant with the $j_1(m=-\frac{1}{2})$ to $j_1(m=\frac{1}{2})$ transition frequency. The atom is initially prepared in the $j_1(m=-\frac{1}{2})$ sublevel and the population of the $j_1(m=\frac{1}{2})$ sublevel is measured. The calculation proceeds as above and one finds the ratio of TQ to SW contributions to be

$$r=c_2[\gamma_2/\gamma_t]\{\lambda[(m_p/m)^{1/2}]\}^2 , \tag{34}$$

where c_2 is a model-dependent factor that ranges from 0.0064 to 0.130. For Na-Xe collisions, $\lambda^2=0.60$; one should be able to see the TQ contribution for $(\gamma_2/\gamma_t)\geq 100$.

There is an addition complication associated with λ-type level schemes that has been neglected in writing Eq. (34). Spontaneous emission also populates the final state under consideration. The contribution from the spontaneous emission terms can provide a flat background that is much larger than that from the TQ terms. To isolate the TQ terms, the fields should be modulated at frequencies that are larger than γ_t, but smaller than $\Gamma_{12}(u)$. If the difference of the modulation frequencies of the two fields is taken to be of order γ_t and if only that part of the signal modulated at twice the difference frequency is monitored, it should be possible to isolate the TQ contribution.

IV. FARADAY ROTATION

In this section, the role of CITEC on the Faraday rotation in an atomic vapor is calculated. A laser field, linearly polarized in the $\hat{\mathbf{x}}$ direction, propagates in the $\hat{\mathbf{z}}$ direction and drives a transition between sublevels of ground and excited states having electronic angular momentum j_1 and j_2, respectively. It is assumed that collisions do not mix the magnetic sublevels of the ground state. On the other hand, it is assumed that the collision rate $\Gamma_{12}(u)$ is sufficiently large to neglect the hyperfine splittings in the ground and excited states [14]. A static magnetic field is applied along the z axis; the Zeeman splitting associated with this field is smaller than all relevant frequencies in the problem.

As a result of the application of the magnetic field, the index of refraction seen by the two circularly polarized components of the linearly polarized field is different and the plane of polarization of the light can rotate as it passes through the vapor. The incident field is written as

$$\begin{aligned}\mathbf{E}(\mathbf{R},t)&=\tfrac{1}{2}E(Z)[\epsilon_q(\epsilon_q)^*]\exp[i(kZ-\Omega t)]+\text{c.c.}\\&=\tfrac{1}{2}E_{+q}(Z)(\epsilon_q)^*\exp[i(kZ-\Omega t)]+\text{c.c.}\\&=\tfrac{1}{2}\mathbf{E}_+(Z)\exp[i(kZ-\Omega t)]+\text{c.c.} ,\end{aligned} \tag{35}$$

where

$$\epsilon_{\pm 1}=\mp(\epsilon_x\pm i\epsilon_y)/\sqrt{2} , \quad \epsilon_0=\epsilon_z \tag{36a}$$

$$\epsilon_{\pm 1}=\mp(\hat{\mathbf{x}}\pm i\hat{\mathbf{y}})/\sqrt{2} , \quad \epsilon_0=\hat{\mathbf{z}} \tag{36b}$$

and $\epsilon=(\epsilon_x,\epsilon_y,\epsilon_z)$ is the (complex) polarization vector of the field. For a field linearly polarized in the x direction, one has

$$\epsilon_q=(-\delta_{q,1}+\delta_{q,-1})/\sqrt{2}\ . \tag{37}$$

This field gives rise to a polarization in the sample which can be written as

$$\mathbf{P}(\mathbf{R},t)=\mathbf{P}_+(Z)\exp[i(kZ-\Omega t)]+\text{c.c.} \tag{38}$$

In the slowly varying amplitude and phase approximation, Maxwell's equations can be used to relate the electric field and polarization through

$$\partial\mathbf{E}_+(Z)/\partial z=(4\pi ik)\mathbf{P}_+(Z)\ . \tag{39}$$

The polarization, in turn, is equal to the average dipole moment per unit volume, which can be related to density-matrix elements in an irreducible tensor notation by

$$\mathbf{P}(\mathbf{R},t)=(1/\sqrt{3})(\epsilon_q)^*(-1)^{j_2-j_1}N\wp^*[\tilde{\rho}^1_q(j_1,j_2)]^*\times\exp[i(kZ-\Omega t)]+\text{c.c.}\ , \tag{40}$$

where $\wp$ is the reduced density-matrix element of the dipole moment operator between states j_2 and j_1, N is the active-atom density, and the tilde indicates a field interaction representation to be defined below. By combining Eqs. (35)–(40), one finds

$$\partial E_{+q}(Z)/\partial z=(1/\sqrt{3})(4\pi ik)(-1)^{j_2-j_1}\times N\wp^*[\tilde{\rho}^1_q(j_1,j_2)]^*\ . \tag{41}$$

It is shown below that, if the initial state is unpolarized, then to first order in the incident field

$$[\tilde{\rho}^1_q(j_1,j_2)]^*=C_qE_{+q}(Z)\ . \tag{42}$$

As a consequence,

$$\partial E_{+q}(Z)/\partial z=-(\alpha_q/2)E_{+q}(Z)\ , \tag{43}$$

where

$$\alpha_q=(2/\sqrt{3})N(4\pi ik)(-1)^{j_2-j_1}\wp^*C_q\ . \tag{44}$$

The field exiting the sample at $Z=L$ is obtained from Eqs. (35) and (43) as

$$\mathbf{E}(L,t)=\tfrac{1}{2}E(Z=0)[e^{-\alpha_1L/2}(\epsilon_1)^*+e^{-\alpha_{-1}L/2}(\epsilon_{-1})^*]\times\exp[i(kL-\Omega t)]+\text{c.c.} \tag{45}$$

In general, the field is elliptically polarized. The plane of polarization is rotated by an angle

$$\phi_f=-\text{Im}[(\alpha_1-\alpha_{-1})L/4]\ , \tag{46}$$

measured from the x axis toward the y axis.

Becquerel's law is valid if

$$\alpha_{\pm1}=\alpha_{\pm1}(\Delta\pm\omega_z)\ , \tag{47}$$

where Δ is the atom-field detuning and ω_z is a Zeeman splitting produced by the magnetic field. If condition (47) holds, then

$$\phi_f\sim-\text{Im}[d\bar{\alpha}/d\Delta]\omega_zL/2\ , \tag{48}$$

where

$$\bar{\alpha}\equiv\alpha_{\pm1}(\omega_z=0)\ . \tag{49}$$

Since $\text{Im}[d\bar{\alpha}/d\Delta]$ is proportional to $-dn_0/d\Delta$, where n_0 is the index of refraction in the absence of the magnetic field, one finds that

$$\phi_f\sim(dn_0/d\Delta)\omega_zL/2\ , \tag{50}$$

which is Becquerel's law. Insofar as $\tilde{\rho}^1_{\pm1}(j_1,j_2)$ is not a function of $(\Delta\pm\omega_z)$, there can be a breakdown of this law.

In an interaction representation defined by $\rho^k_q(j_1,j_2;\mathbf{v})=\tilde{\rho}^k_q(j_1,j_2;\mathbf{v})\exp[-i(kZ-\Omega t)]$, the steady-state solution for $\tilde{\rho}^k_q(j_1,j_2;\mathbf{v})$, to lowest order in the applied field (35) for an initial state that is unpolarized can be obtained from [15]

$$[\Gamma^k_q(\mathbf{v})+i(\Delta-kv_z-\omega^k_q)]\tilde{\rho}^k_q(j_1,j_2;\mathbf{v})=\sum{}'[-\Gamma^{kk'}_{qq'}(1,2,;\mathbf{v})+i\omega^{kk'}_q]\tilde{\rho}^{k'}_{q'}(j_1,j_2;\mathbf{v})+S^k_q(\mathbf{v})\ , \tag{51}$$

where

$$\Gamma^k_q(\mathbf{v})=(\gamma_2/2)+\Gamma^{kk}_{qq}(1,2;\mathbf{v})\ , \tag{52}$$

$$\omega^{kk'}_q=(\beta_0B/\hbar)(-1)^{j_1+j_2+k}(2k'+1)^{1/2}\langle k'q,10|kq\rangle\left[g_{j_2}[j_2(j_2+1)(2j_2+1)]^{1/2}\begin{Bmatrix}k' & 1 & k\\ j_2 & j_1 & j_2\end{Bmatrix}-(-1)^{1+k+k'}g_{j_1}[j_1(j_1+1)(2j_1+1)]^{1/2}\begin{Bmatrix}k' & 1 & k\\ j_1 & j_2 & j_1\end{Bmatrix}\right]\ , \tag{53}$$

$$\omega^k_q\equiv\omega^{kk}_q\ , \tag{54}$$

$$S^k_q(\mathbf{v})=i(\wp^*/2\sqrt{3}\hbar)(-1)^{1+j_2-j_1}(2j_1+1)^{-1}(E_{+q})^*W(\mathbf{v})\delta_{k,1}\ , \tag{55}$$

β_0 is the Bohr magneton, g_j is the Lande g factor, B is the magnitude of the magnetic field applied along the z axis, $\{\begin{smallmatrix} x & x & x \\ x & x & x \end{smallmatrix}\}$ is a 6-j symbol, E_{+q} is the spherical component of the incident field defined by Eqs. (35) and (36), $\Gamma^{kk'}_{qq'}(1,2;\mathbf{v})$ is the collision rate given by Eq. (A1) of Appendix A, and the prime on the summation indicates that the sum excludes diagonal terms with both $k=k'$ and $q=q'$. For an incident field polarized in the x direction, E_{+q} is nonvanishing only for $q=\pm 1$.

We are interested in a solution of Eq. (51) to first order in $\omega^{kk'}_q$. Clearly, if the off-diagonal collisional transfer rates are set equal to zero [that is, preaveraged over $W(\mathbf{v})$], the solution of Eq. (51) to first order in $\omega^{kk'}_q$ is

$$\tilde{\rho}^1_{\pm 1}(j_1,j_2;\mathbf{v})=[\Gamma_1(\mathbf{v})+i(\Delta-kv_z\pm\omega_z)]^{-1}S^1_{\pm 1}\ , \tag{56}$$

where

$$\Gamma_1(\mathbf{v})\equiv\Gamma^1_1(\mathbf{v})=\Gamma^1_{-1}(\mathbf{v})\ ,\quad \omega_z\equiv-\omega^1_1=\omega^1_{-1}\ . \tag{57}$$

It follows immediately from Eq. (56) that Becquerel's law is satisfied since $\tilde{\rho}^1_{\pm 1}(j_1,j_2;\mathbf{v})$ is a function of $(\Delta\pm\omega_z)$. From Eqs. (56), (42)–(44), and (46) one finds a Faraday rotation given by

$$\phi_f=-A_f\omega_z\,\mathrm{Re}\langle[\Gamma_1(\mathbf{v})^*-i(\Delta-kv_z)]^{-2}\rangle\ , \tag{58a}$$

$$A_f=N|\not{\epsilon}|^2(4\pi k)L/12\hbar\ , \tag{58b}$$

where $\langle\ \rangle$ indicates an average over $W(\mathbf{v})$.

Deviations from Becquerel's law can occur when the off-diagonal CITEC rates $\Gamma^{kk'}_{qq'}(1,2;\mathbf{v})$ are nonvanishing. Since the off-diagonal rates are typically much smaller than the diagonal ones, a solution of Eq. (56) to first order in $\Gamma^{kk'}_{qq'}(1,2;\mathbf{v})$ $(k\neq k',\ q\neq q')$ is sought. The $\Gamma^{kk'}_{qq'}(1,2,;\mathbf{v})$ $(k\neq k',\ q\neq q')$ are proportional to $Y^{\kappa}_{q'-q}(\theta_v,\phi_v)$ with κ an even integer ≥ 2 [see Eq. (A1)]. On averaging over ϕ_v, any contribution to $\tilde{\rho}^1_{\pm 1}(j_1,j_2;\mathbf{v})$ will vanish to first order in $\Gamma^{kk'}_{qq'}(1,2;\mathbf{v})$ if $q\neq q'$. As a consequence, we need consider only those terms involving multipole transfer for the same q, i.e.,

$$\Gamma^{kk'}_q(\theta_v)\equiv\Gamma^{kk'}_{qq}(1,2;\mathbf{v})|_{v=u}\ . \tag{59}$$

It follows from Eqs. (A1) and (A13) of Appendix A that there is no multipole transfer unless k or k' is greater than or equal to 2; consequently, there is no multipole transfer for a $j_1=0$ to $j_2=1$ or a $j_1=\frac{1}{2}$ to $j_2=\frac{1}{2}$ transition. As a simplification, all collision rates are evaluated at $v=u$.

Multipole transfer can occur for a $j_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$ transition, typical of the alkali-metal atoms. The appropriate $\Gamma^{kk'}_q(\theta_v)$'s are given by Eqs. (59) and (B16). The cross section for m-changing collisions in the ground state is assumed to be negligibly small, which is a good approximation for alkali-metal–rare-gas collisions [16]. For a $j_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$ transition, k and k' can be equal to 1 or 2 in $\tilde{\rho}^k_q(j_1,j_2;\mathbf{v})$. Equation (56) can be solved for $\tilde{\rho}^2_q(\frac{1}{2},\frac{3}{2};\mathbf{v})$ in terms of $\tilde{\rho}^1_q(\frac{1}{2},\frac{3}{2};\mathbf{v})$ since $S^2_q=0$. The solution is given by

$$\tilde{\rho}^2_{\pm 1}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=\frac{i\omega'_z\mp\Gamma_t(\theta_v)}{\Gamma_2(\mathbf{v})+i(\Delta-kv_z\pm i\omega_{z2})}\tilde{\rho}^1_{\pm 1}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})\ , \tag{60}$$

where

$$\Gamma_2(\mathbf{v})\equiv\Gamma^2_1(\mathbf{v})=\Gamma^2_{-1}(\mathbf{v})\ ,\quad \omega_{z2}\equiv-\omega^2_1=\omega^2_{-1}=\tfrac{9}{7}\omega_z\ , \tag{61}$$

$$\Gamma_t(\theta_v)\equiv\Gamma^{21}_1(1,2;\theta_v)=-\Gamma^{21}_{-1}(1,2;\theta_v)$$
$$=\Gamma^{21}_1(1,2;\theta_v)=-\Gamma^{21}_{-1}(1,2;\theta_v)\ ,$$
$$\omega'_z\equiv-\omega^{21}_1=-\omega^{21}_{-1}=-\omega^{12}_1=-\omega^{12}_{-1}=(\sqrt{3}/7)\omega_z\ . \tag{62}$$

When this solution is substituted back in Eq. (36), Eq. (62) is used, and terms linear in Γ_t and ω_z are retained, one finds

$$\tilde{\rho}^1_{\pm 1}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=\left[\Gamma_1(\mathbf{v})+i(\Delta-kv_z\pm\omega_z)\pm\frac{2i\omega'_z\Gamma_t(\theta_v)}{\Gamma_2(\mathbf{v})+i(\Delta-kv_z)}\right]^{-1}S^1_{\pm 1}(\mathbf{v})\ . \tag{63}$$

As an algebraic simplification, one can set $\Gamma_1(\mathbf{v})=\Gamma_2(\mathbf{v})=\langle\Gamma_1(\mathbf{v})\rangle\equiv\Gamma$, which is approximately true (see Appendix B). Since $|\Gamma_t/\Gamma|\ll 1$ and $|\omega_z/\Gamma|\ll 1$, one can expand (63) to obtain

$$\tilde{\rho}^1_{\pm 1}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})\sim\frac{1}{\mu(v_z)}\left[1\mp\frac{i\omega_z}{\mu(v_z)}\mp\frac{2i\omega'_z\Gamma_t(\theta_v)}{\mu(v_z)^2}\right]S^1_{\pm 1}(\mathbf{v})\ , \tag{64}$$

where

$$\mu(v_z)=\Gamma+i(\Delta-kv_z)\ . \tag{65}$$

Combining Eqs. (64), (46), (42)–(44), and (55), one can obtain the Faraday rotation as

$$\phi_f=\phi_{f1}+\phi_{f2}\ , \tag{66}$$

where

$$\phi_{f1}=-A_f\omega_z\,\mathrm{Re}\langle[\mu(v_z)^*]^{-2}\rangle \tag{67}$$

is that part of the Faraday rotation satisfying Becquerel's law and

$$\phi_{f2}=2A_f\omega'_z\,\mathrm{Re}\langle[\Gamma_t(\theta_v)\mu(v_z)^{-3}]^*\rangle \tag{68}$$

is a correction. Note that one can write

$$\Gamma_t(\theta_v)=\Gamma^{21}_{11}(1,2;\mathbf{v})=\Gamma_tP_2[\cos(\theta_v)]\ . \tag{69}$$

For $W(\mathbf{v})=(\pi u^2)^{-3/2}\exp(-v^2/u^2)$, the integrals implicit in Eqs. (67) and (68) can be evaluated in terms of the plasma dispersion function $Z(\psi)$ defined by

$$Z(\psi)=-(\pi)^{-1/2}\int dz\,e^{-z^2}[\psi\pm z]^{-1}\ ,\quad \mathrm{Im}(\psi)>0\ . \tag{70}$$

One finds

$$\phi_{f1}=-\frac{2A_f\omega_z}{k^2u^2}[1+\mathrm{Re}\{\eta Z(\eta)\}] \tag{71}$$

and

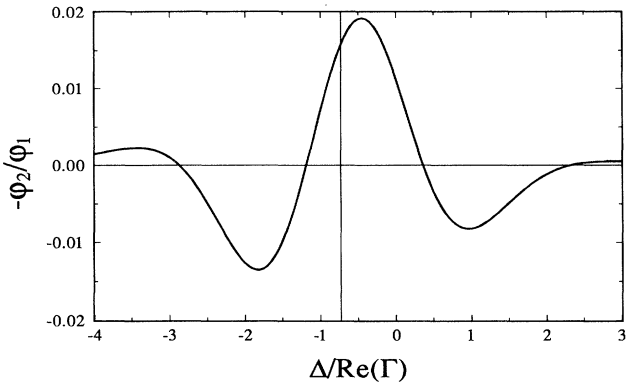

FIG. 6. The deviation of the Faraday rotation from Becquerel's law $(\phi_{\mathrm{Bec}}-\phi_{\mathrm{Far}})/\phi_{\mathrm{Bec}}=-\phi_2/\phi_1$ as a function of $[\Delta/\mathrm{Re}(\Gamma)]$, where ϕ_1 is evaluated at $[\Delta/\mathrm{Re}(\Gamma)]=-0.73$. The perturber to active atom mass ratio is 5.8, the ratio of $\mathrm{Re}(\Gamma)$ to the Doppler width ku is 0.9, and the value of c_3 is 0.1 (see text). A 2% deviation from Becquerel's law is predicted.

$$\phi_{f2}=\frac{\omega_z' A_f}{(ku)^3}\,\mathrm{Re}(\Gamma)\times\{i[\Gamma_t^*/\mathrm{Re}(\Gamma)]\times[\eta(4\eta^2-10)+(4\eta^4-12\eta^2+3)Z(\eta)]\}\ , \tag{72}$$

where

$$\eta=(i\Gamma^*+\Delta)/ku\ . \tag{73}$$

The maximum contribution from ϕ_{f2} arises when $|\Gamma|\sim ku$. For $|\Gamma|\ll ku$, $\phi_{f2}/\phi_{f1}\sim|\Gamma_t|/ku\ll|\Gamma_t/\Gamma|$, while for $|\Gamma|\gg ku$, $\phi_{f2}/\phi_{f1}\sim|\Gamma_t|(ku)^2/|\Gamma|^3\ll|\Gamma_t/\Gamma|$. The ratio ϕ_2/ϕ_1 is proportional to Γ_t/Γ. From Appendix B we have

$$\Gamma_t/\mathrm{Re}(\Gamma)=-c_3\lambda[(m_p/m)^{1/2}](1+0.73i) \tag{74}$$

and c_3 is a model-dependent coefficient that ranges from 0.063 to 0.28. In Fig. 6 the correction to Becquerel's law $\{-\phi_{f2}/\phi_{f1}[\Delta=-\mathrm{Im}(\Gamma)]\}$ is plotted for $\mathrm{Re}[\Gamma]/ku=0.9$, a mass ratio of 5.8 corresponding to Na-Xe collisions, and $c_3=0.1$. The correction is of the order of several percent and should be accessible to experimental verification.

In the limit of very high pressures such that $|\Gamma|\gg ku$, ϕ_2 scales as $[\mathrm{Re}(\Gamma)/ku]^2\ll 1$. Even though ϕ_2 goes to zero, there is still a correction to Becquerel's law of order $(\Gamma_t/\Gamma)^2$. If $\mathrm{Re}(\Gamma)/ku\gg 1$, one can neglect the kv_z term in Eq. (51), solve that equation to second order in the off-diagonal collisional transfer rates, and combine the results with Eqs. (64), (46), (42)–(44), and (55) to obtain a contribution to the Faraday rotation given by

$$\phi_{f3}=-A_f^2\,\mathrm{Re}\left\{\left[(\Gamma+i\Delta)^{-4}\left[2\omega_z'\langle\Gamma_1^{21}(1,2;\mathbf{v})[\Gamma_{11}^{11}(1,2;\mathbf{v})-\Gamma]\rangle+2\omega_z\sum{}'\langle\Gamma_{1q}^{1k}(1,2;\mathbf{v})\Gamma_{q1}^{k1}(1,2;\mathbf{v})\rangle-\sum{}'\omega_q^{kk'}\langle\Gamma_{1q}^{1k}(1,2;\mathbf{v})\Gamma_{q1}^{k'1}(1,2;\mathbf{v})\rangle\right]\right]^*\right\}. \tag{75}$$

Note that terms with $q\neq q'$ contribute in second order. For the parameters chosen in Appendix B, one finds

$$\phi_{f3}=-(A_f^2/5)\{\lambda[(m_p/m)^{1/2}]\}^2\times\mathrm{Re}\{[(\Gamma+i\Delta)^{-4}(i\omega_z)(0.0546+0.170i)]^*\} \tag{76a}$$

for the model in which the collision-induced phase shifts in the levels have opposite signs and

$$\phi_{f3}=-(A_f^2/5)\{\lambda[(m_p/m)^{1/2}]\}^2\times\mathrm{Re}\{[(\Gamma+i\Delta)^{-4}(i\omega_z)(0.304+0.934i)]^*\} \tag{76b}$$

for the model in which the phase shifts have the same sign and are of comparable magnitude. The correction to Becquerel's law $\{-\phi_{f3}/\phi_{f1}[\Delta=-\mathrm{Im}(\Gamma)]\}$ ranges from 0.2% to 4% for a mass ratio $m_p/m=1.55$ corresponding to Rb-Xe collisions, so it is unlikely that this contribution

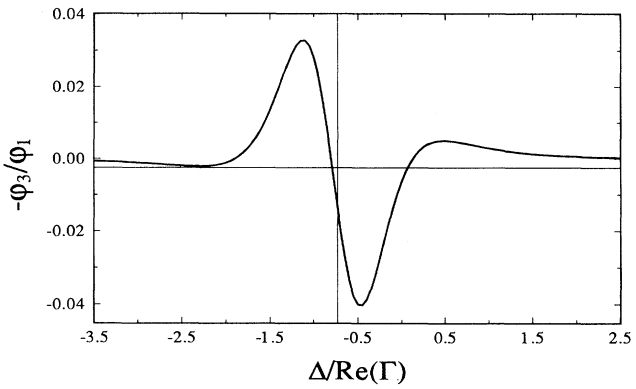

FIG. 7. The deviation of the Faraday rotation from Becquerel's law $(\phi_{\mathrm{Bec}}-\phi_{\mathrm{Far}})/\phi_{\mathrm{Bec}}=-\phi_3/\phi_1$ as a function of $[\Delta/\mathrm{Re}(\Gamma)]$, where ϕ_1 is evaluated at $[\Delta/\mathrm{Re}(\Gamma)]=-0.73$. This graph differs from Fig. 6 in that the pressure is assumed to be sufficiently high $[\mathrm{Re}(\Gamma)\gg ku]$ that terms linear in the collisional transfer rates are negligible, and only terms quadratic in these rates contribute in this graph. The perturber to active atom mass ratio is 1.55. The deviation of 4% is for a model in which there is a fortuitous phase cancellation of collisional shift. If the collisional phase shifts associated with the ground and excited states have opposite signs, the correction would be of order 0.2%.

is dominating the experimentally measured deviation from Becquerel's law measured by Kristensen, van Eijkelenborg, and Woerdman [7]. Moreover, the line shape of the correction as a function of detuning (see Fig. 7) differs qualitatively from the experimental results.

V. SUMMARY AND DISCUSSION

It has been shown that collisional transfer of electronic state coherence can lead to new features in the spectral response of an atomic vapor. Two examples were considered, the nonlinear spectroscopy of a three-level atom and the deviation from Becquerel's law in an atomic vapor. In both cases, collisional transfer rates $\Gamma_t(\mathbf{v})$ are responsible for the observed features, despite the fact that these rates vanish when averaged over the active-atom velocity distribution. To properly account for the collisional transfer, it is necessary to calculate the appropriate line shape as a function of $\Gamma_t(\mathbf{v})$ before carrying out the average over the active-atom velocity distribution. Since the collisional transfer rates are generally much smaller than the "diagonal" decay rates these effects tend to be relatively small.

All effects related to collisional velocity changes have been neglected. Such effects must be included for a consistent picture of angular momentum conservation, since any changes in the internal angular momenta of the colliding atoms must be compensated by a corresponding change in the angular momentum associated with the center-of-mass variables of each of the atoms. (In the work of Bacon *et al.* [4], a velocity dependence of $\Gamma^{m_1'm_2'}_{m_1m_2}(1,2;\mathbf{v})$ $[(m_1'-m_1)=(m_2'-m_2)]$ was included in the analysis.) Although formal expressions are available [17] that treat both the internal and external variables in a consistent manner, little progress in a practical evaluation of these formulas has been made. It is known that the retention of electronic state coherence following collisions is often associated with diffractive scattering [18]. Since scattering in the diffractive cone is inconsistent with changes in angular momentum much greater than $\hbar$, additional calculations are needed to prove conclusively that $\Gamma^{kk'}_{qq'}(1,2;\mathbf{v})$ does not vanish for $q\neq q'$ when effects related to changes in the atoms' center-of-mass velocities are included.

Collisional transfer of electronic state coherence can play a role in modifying signals in both the frequency and time domains. For signals that are proportional to the absolute square of the atomic polarization, it is important to remember that the polarization is averaged over the active-atom velocity distribution before the absolute square is taken. As a consequence, effects linear in the transfer rates $\Gamma_t(\mathbf{v})$ vanish. For example, it would be impossible to observe a photon echo on the $j_1=0$ to $j_2=1$, $m_2=1$ transition of Fig. 1 since the rate of coherence transfer to these levels from the coherence $\rho_{0,-1}(1,2;\mathbf{v})$ is, on average, zero. On the other hand, in stimulated echo and four-wave-mixing experiments, where the signal can be proportional to $|\Gamma_t(\mathbf{v})|^2$, collisional transfer of electronic state coherence can lead to new features in the line shapes.

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APPENDIX A: RATE COEFFICIENTS

Expressions for $\Gamma^{kk'}_{qq'}(j,j;\mathbf{v})$ have been derived previously [8–11]. The corresponding derivation for $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$ is identical and the result can be stated as

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})=-N_p(-1)^{m_2-m_2'+q''-q}\langle j_1m_1,j_2-m_2|kq''\rangle\langle j_1m_1',j_2-m_2'|k'q''\rangle \times\langle k-q'',k'q''|K0\rangle\langle k-q,k'q'|KQ\rangle[4\pi/(2K+1)]^{1/2}Y^K_Q(\theta_v,\phi_v)I_K(m_1,m_1',m_2,m_2')\,, \tag{A1}$$

where

$$I_K(m_1,m_1',m_2,m_2') =(\pi u_p^2)^{-3/2}\int d\mathbf{v}_r F_K(2vv_r/u_p^2)\exp[-(v_r^2+v^2)/u_p^2] \times\int_0^\infty(2\pi bdb)v_r M^{m_1'm_2'}_{m_1m_2}(b,v_r,\Omega_0)\,, \tag{A2}$$

$$F_K(a)=\tfrac{1}{2}\int_{-1}^{1}dx\,e^{-ax}P_K(x)\,, \tag{A3}$$

N_p is the perturber density, u_p is the most probable perturber speed, θ_v and ϕ_v are the polar angles of $\mathbf{v}$ relative to the laboratory frame, P_K is a Legendre polynomial, and

$$M^{m_1'm_2'}_{m_1m_2}(b,v_r,\Omega_0) =S_{m_1m_1'}(j_1;b,v_r,\Omega_0)[S_{m_2m_2'}(j_2;b,v_r,\Omega_0)]^* -\delta_{m_1m_1'}\delta_{m_2m_2'}\,, \tag{A4}$$

where the $S_{mm'}(j;b,v_r,\Omega_0)$ are S-matrix elements for an m' to m transition in state j for a collision geometry Ω_0 in which the impact parameter lies along the x axis and the initial relative velocity is in the z direction. Gaussian velocity distributions have been taken for the active atoms and perturbers. One notes immediately that if $(\theta_v,\phi_v)=(0,0)$, $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$ vanishes unless $(q-q')=0$; an active atom moving along the quantization axis experiences an axially symmetric perturber velocity distribution which cannot, on average, change its z component

of angular momentum. It is assumed throughout that the atoms move on straight-line paths. For $(v/u_p)\ll 1$, the active atoms experience an isotropic perturber velocity distribution; in that limit, $F_K(a)\propto\delta_{K0}$ and, as a consequence, the decay rates $\Gamma^{kk'}_{qq'}(j_1,j_2;0)=\Gamma^k(j_1,j_2)\delta_{qq'}\delta_{kk'}$ are diagonal in k and q and are independent of q [6]. For $q=q'$, one sets

$$\Gamma^{kk'}_q(j_1,j_2;\mathbf{v})\equiv\Gamma^{kk'}_{qq}(j_1,j_2;\mathbf{v})\ . \tag{A5}$$

In the magnetic state basis, one has

$$\Gamma^{m_1'm_2'}_{m_1m_2}(j_1,j_2;\mathbf{v})=(-1)^{m_2-m_2'}\langle j_1m_1,j_2-m_2|kq\rangle \times\langle j_1m_1',j_2-m_2'|k'q'\rangle\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})\ . \tag{A6}$$

In many cases of practical interest, collisions do not change the value of m in the ground state, that is,

$$S_{m_1m_1'}(j_1;b,v_r,\Omega_0)=S(j_1;b,v_r,\Omega_0)\delta_{m_1m_1'}\ . \tag{A7}$$

In that case, Eq. (A1) reduces to

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v};\delta m_1=0)=-N_p(-1)^{q+2j_2-j_1-m_2}[(2k+1)(2k'+1)]^{1/2}\langle j_2-m_2,j_2m_2|K0\rangle \times\langle k-q,k'q'|KQ\rangle\begin{Bmatrix}k & k' & K\\ j_2 & j_2 & j_1\end{Bmatrix}[4\pi/(2K+1)]^{1/2}Y^K_Q(\theta_v,\phi_v)I_K(m_2,m_2)\ , \tag{A8}$$

where I_K is now evaluated by replacing $S_{m_1m_1'}(j_1;b,v_r,\Omega_0)$ with $S(j_1;b,v_r,\Omega_0)$ in Eq. (A4). The corresponding equation in the m basis takes on the remarkably simple form

$$\Gamma^{m_1'm_2'}_{m_1m_2}(j_1,j_2;\mathbf{v})=\Gamma^{m_2'}_{m_2}(j_1,j_2;\mathbf{v})\delta_{m_1m_1'}\ , \tag{A9}$$

$$\Gamma^{m_2'}_{m_2}(j_1,j_2;\mathbf{v})=-N_p(-1)^{q+j_1+m_2}\langle j_2-m_2,j_2m_2'|K-Q\rangle[4\pi/(2k+1)]^{1/2}Y^K_Q(\theta_v,\phi_v) \times[(-1)^{j_2+m_2''}\langle j_2-m_2'',j_2m''|K0\rangle I_K(m_2'',m_2'')]\ . \tag{A10}$$

In Appendix B, values for the S-matrix elements and Γ's are calculated assuming a dipole-dipole interaction between the active atoms and perturbers. Some general comments can be made at this point. By taking the complex conjugate of Eqs. (3) and (4), one can show that

$$\Gamma^{m_1'm_2'}_{m_1m_2}(j_1,j_2;\mathbf{v})=[\Gamma^{m_2'm_1'}_{m_2m_1}(j_2,j_1;\mathbf{v})]^*\ , \tag{A11}$$

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})=(-1)^{q-q'}[\Gamma^{kk'}_{-q-q'}(j_2,j_1;\mathbf{v})]^*\ . \tag{A12}$$

From symmetry on reflection in planes containing the z axis it follows that [8–11]

$$S_{mm'}(j;b,v_r,\Omega_0)=(-1)^{m-m'}S_{-m-m'}(j;b,v_r,\Omega_0)\ , \tag{A13}$$

from which it follows that only terms with K even enter the sums in Eqs. (A1), (A8), and (A10). Equation (A13) does not result in any relationships among the $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$'s or $\Gamma^{m_1'm_2'}_{m_1m_2}(j_1,j_2;\mathbf{v})$'s; however, it does follow from Eqs. (A13), (A1), (A6), (A8), and (A10) that

$$\Gamma^{kk'}_q(j_1,j_2;\mathbf{v})=(-1)^{k+k'}\Gamma^{kk'}_{-q}(j_1,j_2;\mathbf{v})\ , \tag{A14a}$$

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v};\delta m_1=0)=(-1)^{k+k'+q-q'}\Gamma^{k'k}_{-q'-q}(j_1,j_2;\mathbf{v};\delta m_1=0)\ , \tag{A14b}$$

$$\Gamma^{m_2'}_{m_2}(j_1,j_2;\mathbf{v})=(-1)^{m_2-m_2'}\Gamma^{-m_2}_{-m_2'}(j_1,j_2;\mathbf{v})\ . \tag{A14c}$$

Moreover, for straight-line paths, one can show that, in addition to Eq. (A13), the S-matrix elements satisfy [10]

$$S_{mm'}(j;b,v_r,\Omega_0)=(-1)^{m-m'}S_{m'm}(j;b,v_r,\Omega_0)\ , \tag{A15}$$

from which it follows that

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})=(-1)^{k+k'+q-q'}\Gamma^{k'k}_{-q'-q}(j_1,j_2;\mathbf{v})\ , \tag{A16a}$$

$$\Gamma^{m_1'm_2'}_{m_1m_2}(j_1,j_2;\mathbf{v})=(-1)^{m_2-m_2'+m_1-m_1'}\Gamma^{-m_1-m_2}_{-m_1'-m_2'}(j_1,j_2;\mathbf{v})\ . \tag{A16b}$$

Combining Eqs. (A6) and (A16a), one finds

$$\Gamma^{kk'}_q(j_1,j_2;\mathbf{v})=\Gamma^{k'k}_q(j_1,j_2;\mathbf{v})\ . \tag{A17}$$

From the Clebsch-Gordon coefficients appearing in Eq. (A1) and the fact that only even values of K enter the sum, one can deduce that the multipole transfer rates $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v})$ $(k\neq k')$ vanish for $j_1=0$ to $j_2=1$ or for $j_1=\frac{1}{2}$ to $j_2=\frac{1}{2}$ transitions. It also follows from Eq. (A8) that $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v};\delta m_1=0)$ is diagonal in both k and q for a $j_1=\frac{1}{2}$ to $j_2=\frac{1}{2}$ transition, implying that CITEC does not lead to violations in Becquerel's law for such a transition.

APPENDIX B: ESTIMATE OF THE TRANSFER RATES

In this appendix a rough estimate of the transfer rates for a$(l_1=0,\ s=0,\ j_1=0)$ to $(l_2=1,\ s=0,\ j_2=1)$ and a $(l_1=0,\ s=\frac{1}{2},\ j_1=\frac{1}{2})$ to $(l_2=1,\ s=\frac{1}{2},\ j_2=\frac{3}{2})$ transition is obtained assuming a dipole-dipole interaction between the active atoms and perturbers (such as rare-gas atoms) whose ground state is an $(l_1'=0,\ s'=0,\ j_1'=0)$ state. The interaction potential between the active atom and per-

turber is expressed conveniently as [19]

$$U(t)=-(\tfrac{2}{15})^{1/2}\frac{(4\pi)^{3/2}}{R(t)^3}Y_Q^2[\theta(t),\phi(t)]^*V_Q^2(1,1)\ , \tag{B1}$$

where $R(t)$ is the active-atom–perturber internuclear separation, (θ,ϕ) are the polar angles of the relative velocity during the collision, and $V_Q^2(1,1)$ is an irreducible tensor operator of rank-two expressed in a *composite* basis of active-atom and perturber states, i.e.,

$$V_Q^2(1,1)=\langle 1q,1q'|2Q\rangle T_q^1 T'^1_{q'}\ , \tag{B2}$$

where T and T' are irreducible tensors of rank-one associated with the dipole moment operators of the active atom and perturber, respectively. For the reference geometry in which the relative velocity $\mathbf{v}_r$ is in the $\hat{\mathbf{z}}$ direction and the impact parameter $\mathbf{b}$ in the $\hat{\mathbf{x}}$ direction, one has

$$\begin{aligned}&\cos[\theta(t)]=v_r t/R(t)\ ,\quad \sin[\theta(t)]=b/R(t)\ ,\\ &R(t)=(b^2+v_r^2t^2)^{1/2}\ ,\quad \phi(t)=0\end{aligned} \tag{B3}$$

assuming straight-line paths for the atoms.

Given the potential (B1), we must calculate the time evolution of probability amplitudes $a(JM;t)$ in a composite angular momentum basis for the active atoms and perturbers. In other words, the state vector for the system is expanded as

$$\begin{aligned}|\psi\rangle=&a(j,j';JM;t)\langle jm,j'm'|JM\rangle|jm\rangle|j'm'\rangle\\ &\times\exp(-i\omega_J t)\ ,\end{aligned} \tag{B4}$$

where unprimed variables refer to the active atom, primed to the perturber, and ω_J is the sum of energies of states $|jm\rangle$ and $|j'm'\rangle$. The initial conditions are given by

$$a(j,j';JM;t=-\infty)=a_0(j_0m)\delta_{jj_0}\delta_{j'0}\delta_{Jj}\delta_{Mm}\ . \tag{B5}$$

In other words, the active atom starts in state $|j_0\rangle$, while the perturber starts in its ground state having angular momentum $j'=0$. The initial (and final) composite state labels are the same as those for the active atom since $j'=0$ for these states. The active-atom–perturber interaction proceeds via virtual intermediate states (see below). At time $t=\infty$, one finds final state amplitudes given by

$$a(j_0,j'=0;j_0m;t=\infty)=S_{mm'}(j_0)a_0(j_0m')\ , \tag{B6}$$

which defines the S-matrix elements. Note that $j_0=j_1,j_2$ in our problem.

Owing to dipole selection rules, the potential (B1) does not directly couple levels within the initial-state manifold. One must iterate the equation $i\hbar\dot{a}(JM;t)=\langle JM|U|J'M'\rangle a(J'M';t)\exp(i\omega_{JJ'}t)$ through a set of intermediate virtual states to arrive at the vector equation [5]

$$i\hbar\dot{\mathbf{a}}(j_0)=\mathbf{T}(j_0,t)\mathbf{a}(j_0)\ , \tag{B7}$$

where $\mathbf{a}(j_0)$ is a column vector having elements $a(j_0,j'=0;j_0m;t)$ and $\mathbf{T}(j_0;t)$ is a matrix having matrix elements

$$\begin{aligned}T_{mm'}(j_0;t)=&\frac{2(4\pi)^3}{[15R(t)]^6}(2J+1)^{-1}(\hbar\omega_{j_0J})^{-1}Y_Q^2[\theta(t),0]^*Y_{Q'}^2[\theta(t),0]\\ &\times\langle JM,2Q|j_0m\rangle\langle JM,2Q'|j_0m'\rangle|\langle j_0,j'=0;j_0\|V^{(2)}(1,1)\|j,j';J\rangle|^2\ ,\end{aligned} \tag{B8}$$

where the last factor is a reduced matrix involving the intermediate virtual state $|j,j';JM\rangle$. In general, Eq. (B7) must be solved numerically to get S-matrix elements as a function of b and v_r. An approximate solution, sufficient for our purposes here [5], can be obtained if the noncommunitivity of $\mathbf{T}(t)$ and $\mathbf{T}(t')$ for $t\neq t'$ is neglected. In that case,

$$\mathbf{S}(j_0;b,v_r)=\exp\left[(i\hbar)^{-1}\int_{-\infty}^{\infty}\mathbf{T}(b,v_r;j_0;t)dt\right]\ , \tag{B9}$$

where $\mathbf{S}$ is a matrix having elements $S_{mm'}$ and the explicit dependence on b, v_r, and j_0 has been indicated. Equations (B7) and (B9) can be expressed in terms of dimensionless variables if one defines

$$|V_0|^2\equiv|\langle j_2,j'=0;j_2\|V^{(2)}(1,1)\|\bar{j},\bar{j}';\bar{J}\rangle|^2 \tag{B10}$$

for some arbitrary intermediate state. Then, Eq. (B9) may be rewritten as

$$\mathbf{S}(j_0;b,v_r)=\exp\left[-i(C/b^5v_r)\int_{-\infty}^{\infty}\tilde{\mathbf{T}}(j_0;x)dx\right]\ , \tag{B11}$$

where

$$C=(128\pi^3/15)(2\bar{J}+1)^{-1}|\hbar\omega_{j_0\bar{J}}|^{-1}|V_0|^2/\hbar\ . \tag{B12}$$

$\tilde{\mathbf{T}}$ is a matrix having elements

$$\begin{aligned}\tilde{T}_{mm'}(j_0;x)=&(1+x^2)^{-3}[(2\bar{J}+1)/(2J+1)](|\omega_{j_0\bar{J}}|/\omega_{j_0J})Y_Q^2[\theta(x),0]^*Y_{Q'}^2[\theta(x),0]\\ &\times\langle JM,2Q|j_0m\rangle\langle JM,2Q'|j_0m'\rangle|\langle j_0,j'=0;j_0\|V^{(2)}\|j,j';J\rangle|^2/|V_0|^2\end{aligned} \tag{B13}$$

and

$$\cos[\theta(x)]=x/(1+x^2)^{1/2}\ ,\quad \sin[\theta(x)]=1/(1+x^2)^{1/2}\ . \tag{B14}$$

With some additional changes of variables, the transfer rates for collisions which do not change m in state $|j_1\rangle$, given by Eqs. (A8) and (A10), can be written

$$\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v};\delta m_1=0)=N_p C^{2/5}u_p^{3/5}(-1)^{q+j_2+j_1}[(2k+1)(2k'+1)]^{1/2}\langle k-q,k'q'|KQ\rangle \times\begin{Bmatrix}k & k' & K\\ j_2 & j_2 & j_1\end{Bmatrix}[4\pi/(2K+1)]^{1/2}Y^K_Q(\theta_v,\phi_v)i_K(v/u_p)M_K(j_1,j_2) \tag{B15}$$

and

$$\Gamma^{m_2'}_{m_2}(j_1,j_2;\mathbf{v})=N_p C^{2/5}u_p^{3/5}(-1)^{j_1+m_2'} \times\langle j_2-m_2,j_2m_2'|K-Q\rangle \times[4\pi/(2k+1)]^{1/2}Y^K_Q(\theta_v,\phi_v) \times i_K(v/u_p)M_K(j_1,j_2)\ , \tag{B16}$$

where

$$i_K(y)=(\pi)^{-3/2}\int d\mu\, F_K(2\mu y)\mu^{3/5}\exp[-(\mu^2+y^2)]\ , \tag{B17}$$

$$M_K(j_1,j_2)=(2\pi/5)\int_0^\infty d\eta\,\eta^{-7/5}M_K(j_1,j_2;\eta)\ , \tag{B18}$$

$$M_K(j_1,j_2;\eta)=(-1)^{j_2+m_2}\langle j_2-m_2,j_2m_2|K0\rangle \times[1-S(j_1;\eta)S_{m_2m_2}(j_2,\eta)^*]\ , \tag{B19}$$

and

$$\mathbf{S}(j_0;\eta)=\exp\left[-i\eta\int_{-\infty}^{\infty}\bar{\mathbf{T}}(j_0;x)dx\right]\ . \tag{B20}$$

The problem reduces to a calculation of M_K and $i_K(y)$.

For $j_1=0$ to $j_2=1$ and $j_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$ transitions, only terms with $K=0,2$ contribute to the sum in Eq. (B15). The values of F_K needed in Eq. (B17) can be obtained from Eq. (A3) as

$$F_0(a)=\sinh(a)/a\ ,\qquad F_2(a)=\frac{(a^2+3)\sinh(a)}{a^3}-\frac{3\cosh(a)}{a^2}\ . \tag{B21}$$

It is possible to express the resulting integrals (B17) for i_K in terms of parabolic cylinder functions, but the rather lengthy expressions are not given here. For $y<1$,

$$i_0(y)\sim 1.05[1+(y^2/5)+(7y^4/250)]\ ,\qquad i_2(y)\sim 0.505y^2[1-(y^2/5)+0.0379y^4]\ , \tag{B22a}$$

while, for $y\gg 1$,

$$i_0(y)\sim y^{3/5}[1+(6/25y^2)]\ ,\qquad i_2(y)\sim y^{3/5}[1-(1.26/y^2)+(0.90/y^4)]\ . \tag{B22b}$$

In the text, i_K is evaluated at $v=u$ ($y=u/u_p$), the most probable active atom speed. A graph of i_2/i_0 as a function of $m_p/m=(u/u_p)^2$ is shown in Fig. 4. For $y=0$, the active atoms see an isotropic distribution of perturbers and $\Gamma^{kk'}_{qq'}(j_1,j_2;\mathbf{v}=0;\delta m_1=0)$ is diagonal in both k and q.

To evaluate $M_K(j_1,j_2)$, we first use Eqs. (B19) and (B20) to write

$$M_0(\tfrac{1}{2},\tfrac{3}{2};\eta)=2-e^{-i\eta\phi_1}[S_{3/2,3/2}(\tfrac{3}{2};\eta)+S_{\frac{1}{2},\frac{1}{2}}(\tfrac{3}{2};\eta)]^*\ , \tag{B23a}$$

$$M_2(\tfrac{1}{2},\tfrac{3}{2};\eta)=-e^{-i\eta\phi_1}[S_{3/2,3/2}(3/2;\eta)-S_{1/2,1/2}(3/2;\eta)]^*\ , \tag{B23b}$$

$$M_0(0,1;\eta)=\{3-e^{-i\eta\phi_1}[2S_{11}(1;\eta)+S_{00}(1;\eta)]^*\}/\sqrt{3}\ , \tag{B23c}$$

$$M_2(0,1;\eta)=-(\tfrac{2}{3})^{1/2}e^{-i\eta\phi_1}[S_{11}(1;\eta)-S_{00}(1;\eta)]^*\ , \tag{B23d}$$

where

$$e^{-i\eta\phi_1}=S(j_1;\eta)\ , \tag{B24}$$

$$\phi_1=\tfrac{1}{9}(2\bar{J}+1)(|\omega_{j_1\bar{J}}|/\omega_L)(|\langle l_1=0||T^{(1)}||l=1\rangle \times\langle l_1'=0||T'^{(1)}||l'=1\rangle|^2/|V_0|^2) \times\sum_Q\int_{-\infty}^{\infty}(1+x^2)^{-3}|Y^2_Q[\theta(x),0]|^2dx\ , \tag{B25}$$

and the reduced matrix elements have been reexpressed in terms of the single atom reduced matrix elements, taking into account the fact that both $l_1=0$ and $l_1'=0$. The frequency ω_L, equal to $(\omega_{l_1l}+\omega_{l_1'l'})$, is negative if state j_1 is the ground state. In the following, it is assumed that ω_L is negative.

The S-matrix elements in Eq. (B23) must be calculated numerically using Eq. (B11). Implicit in their evaluation is a sum over all possible intermediate states. To arrive at a numerical estimate of the ratios of the various Γ's, I make the simplifying assumption that a single intermediate state (j,j') dominates the sum; both $\omega_{\bar{J}J}$ and $|V_0|^2$ appearing in Eqs. (B10) and (B12) are evaluated for this intermediate state using the maximum value of $\bar{J}$ associated with the composite (j,j') states. For the $j_1=\frac{1}{2}$ to $j_2=\frac{3}{2}$ transition, the intermediate manifold is taken as $|j=\frac{1}{2},j'=1;J=\frac{1}{2},\frac{3}{2}\rangle$ $(\bar{J}=\frac{3}{2})$, while, for the $j_1=0-j_2=1$ transition, the intermediate state is taken as $|j=0,j'=1;J=\bar{J}=1\rangle$. One can then integrate over x in Eq. (B11), numerically evaluate the resulting $\mathbf{S}$ matrix, and substitute these values in Eqs. (B23) to obtain

$$M_0(\tfrac{1}{2},\tfrac{3}{2};\eta)=2-e^{-i\eta\phi_1}[e^{i\eta\phi_{21}(3/2)}+e^{i\eta\phi_{22}(3/2)}]\ , \tag{B26a}$$

$$M_2(\tfrac{1}{2},\tfrac{3}{2};\eta)=-0.327e^{-i\eta\phi_1}(e^{i\eta\phi_{21}(3/2)}-e^{i\eta\phi_{22}(3/2)}]\ , \tag{B26b}$$

$$M_0(0,1;\eta)=3-e^{-i\eta\phi_1}[e^{i\eta\phi_{21}(1)}+e^{i\eta\phi_{22}(1)}$$

$$+e^{i\eta\phi_{23}(1)}]/\sqrt{3}\ , \tag{B26c}$$

$$M_2(0,1;\eta)=-(\tfrac{2}{3})^{1/2}e^{-i\eta\phi_1}\times[(\tfrac{1}{2})(e^{i\eta\phi_{21}(1)}+e^{i\eta\phi_{22}(1)})-e^{i\eta\phi_{23}(1)}]\ , \tag{B26d}$$

where

$$\phi_{21}(\tfrac{3}{2})=-0.424\ ,\quad \phi_{22}(\tfrac{3}{2})=-0.138\ ,$$
$$\phi_{21}(1)=-0.820\ ,$$
$$\phi_{22}(1)=-0.234\ ,$$
$$\phi_{23}(1)=-0.351 \tag{B27}$$

(the sign of the $\omega_{j_2\bar{J}}$ has been taken as negative).

To carry out the integration over η in Eq. (B18), some assumption on the relative values of ϕ_1 and $\phi_{ij}(j_2)$ is needed. Two models are adopted. In the first model, $\phi_1=0$, on the assumption that the scattering cross section for state j_2 is much larger than that for state j_1. [Except for an overall multiplicative factor, this model leads to collision rates that are identical to those for a model in which $\omega_{j_2\bar{J}}$ is positive (phase shifts of opposite sign for states j_1 and j_2).] With $\phi_1=0$, numerical integration of Eq. (B17) yields

$$M_0(\tfrac{1}{2},\tfrac{3}{2})=(2\pi/5)(3.50+2.54i)\ , \tag{B28a}$$
$$M_2(\tfrac{1}{2},\tfrac{3}{2})=(2\pi/5)(0.266+0.194)\ , \tag{B28b}$$
$$M_0(0,1)=(2\pi/5)(6.45+4.69i)/\sqrt{3}\ , \tag{B28c}$$
$$M_2(0,1)=(2\pi/5)(\tfrac{2}{3})^{1/2}(0.251+0.182i)\ . \tag{B28d}$$

In the second model, I try to estimate the maximum ratio that M_2/M_0 can achieve by some fortuitous choice of ϕ_1. For the $\frac{1}{2}$ to $\frac{3}{2}$ transition, I set $\phi_1=\phi_{22}(\frac{3}{2})$ and, for the 0 to 1 transition, $\phi_1=\phi_{23}(1)$. In that limit, one finds

$$M_0(\tfrac{1}{2},\tfrac{3}{2})=(2\pi/5)(1.83+1.33i)\ , \tag{B29a}$$
$$M_2(\tfrac{1}{2},\tfrac{3}{2})=0.327M_0(\tfrac{1}{2},\tfrac{3}{2})\ , \tag{B29b}$$
$$M_0(0,1)=(2\pi/5)(3.50+0.687i)/\sqrt{3}\ , \tag{B29c}$$
$$M_2(0,1)=(1/\sqrt{2})M_0(0,1)\ . \tag{B29d}$$

It remains only to calculate the various Γ's needed in the text using Eqs. (B15) and (B16). The results are expressed in terms of the ratio

$$\lambda(v/u_p)=i_2(v/u_p)/i_0(v/u_p)\ . \tag{B30}$$

Model 1: $\phi_1=0$.

$$\Gamma_1^{11}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(1.75+1.27i)+\lambda(0.0632+0.046i)D_0^2(\theta_v,\phi_v)]\ , \tag{B31a}$$
$$\Gamma_1^{22}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(1.75+1.27i)-\lambda(0.0632+0.046i)D_0^2(\theta_v,\phi_v)]\ , \tag{B31b}$$
$$\Gamma_1^{21}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=-A\lambda(0.1102+0.080i)D_0^2(\theta_v,\phi_v)\ , \tag{B31c}$$
$$\Gamma_1^1(0,1;\mathbf{v})=\Gamma_{-1}^1(0,1;\mathbf{v})=A[(2.15+1.56i)+\lambda(0.084+0.061i)D_0^2(\theta_v,\phi_v)]\ , \tag{B31d}$$
$$\Gamma_1^{-1}(0,1;\mathbf{v})=A\lambda(0.205+0.148i)D_2^2(\theta_v,\phi_v)\ , \tag{B31e}$$
$$\Gamma_{3/2}^{3/2}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(1.75+1.27i)+\lambda(0.126+0.092i)D_0^2(\theta_v,\phi_v)]\ , \tag{B31f}$$
$$\Gamma_{1/2}^{1/2}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(1.75+1.27i)-\lambda(0.126+0.092i)D_0^2(\theta_v,\phi_v)]\ , \tag{B31g}$$
$$\Gamma_{3/2}^{1/2}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=-A\lambda(0.205+0.148i)D_1^2(\theta_v,\phi_v)\ . \tag{B31h}$$

Model 2: $\phi_1=\phi_{22}(\frac{3}{2})$ *and* $\phi_1=\phi_{23}(1)$.

$$\Gamma_1^{11}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(0.915+0.665i)+\lambda(0.1492+0.108i)D_0^2(\theta_v,\phi_v)]\ , \tag{B32a}$$
$$\Gamma_1^{22}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(0.915+0.665i)-\lambda(0.1492+0.108i)D_0^2(\theta_v,\phi_v)]\ , \tag{B32b}$$
$$\Gamma_1^{21}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=-A\lambda(0.259+0.188i)D_0^2(\theta_v,\phi_v)\ , \tag{B32c}$$
$$\Gamma_1^1(0,1;\mathbf{v})=\Gamma_{-1}^1(0,1;\mathbf{v})=A[(1.17+0.229i)+\lambda(0.583+0.115i)D_0^2(\theta_v,\phi_v)]\ , \tag{B32d}$$
$$\Gamma_1^{-1}(0,1;\mathbf{v})=A\lambda(1.43+0.280i)D_2^2(\theta_v,\phi_v)\ , \tag{B32e}$$
$$\Gamma_{3/2}^{3/2}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(0.915+0.665i)+\lambda(0.299+0.217i)D_0^2(\theta_v,\phi_v)]\ , \tag{B32f}$$
$$\Gamma_{1/2}^{1/2}(\tfrac{1}{2},\tfrac{3}{2};\mathbf{v})=A[(0.915+0.665i)-\lambda(0.299+0.217i)D_0^2(\theta_v,\phi_v)]\ , \tag{B32g}$$
$$\Gamma_{3/2}^{1/2}(\tfrac{1}{2},\tfrac{3}{2}\mathbf{v})=-A\lambda(0.422+0.307i)D_1^2(\theta_v,\phi_v)\ , \tag{B32h}$$

where

$$A=(8\sqrt{\pi}/5)C^{2/5}u_p^{3/5}i_0(v/u_p) \tag{B33}$$

and

$$D_Q^2(\theta_v,\phi_v)=(4\pi/5)^{1/2}Y_0^2(\theta_v,\phi_v)\ . \tag{B34}$$

Note that the "homogeneous" part of the diagonal (in both k and q or in m) collision rates is generally much larger than the part varying as $D_0^2(\theta_v,\phi_v)$. It is on this basis that, to a first approximation, one can take all the diagonal rates (or a given j_1 and j_2) to be equal and independent of (θ_v,ϕ_v).

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