Ramsey fringes in laser-assisted collisions

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It is shown theoretically that Ramsey fringes can be produced when a laser-assisted reaction of the form $A_2+A'_1+\hbar\Omega\rightarrow A_1+A'_2$ is driven by a pair of ultrafast radiation pulses, each of whose temporal widths is less than the duration τ_c of a collision between the A and A' atoms. The excitation profile of the laser-assisted collision is calculated as a function of detuning of the laser field frequency from the initial- to final-state transition frequency. For radiation pulses separated by time T, Ramsey fringes appear separated in frequency by T^{-1}. The modulation depth and shift of the central Ramsey fringe as a function of (T/τ_c) provide information about the collisional interaction. Both the weak- and strong-field regions are considered and comparison with laser-assisted collisions using excitation pulses having temporal widths greater than τ_c is made.

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I. INTRODUCTION

Laser-assisted collisions refer to reactions that require the simultaneous action of a collisional interaction and an interaction with a radiation field. These reactions have been divided into two categories, *collisionally aided radiative excitation* (CARE) and *light-induced collisional energy transfer* (LICET) [1]. CARE reactions are of the form

$$A_1+A'_1+\hbar\Omega\rightarrow A_2+A'_1 \;. \qquad (1)$$

Two atoms A and A' collide in the presence of a radiation field having frequency Ω. The field is detuned from a resonant transition frequency in atom A, but, as a result of the combined collisional-radiative interaction, atom A is excited to state $|2\rangle$ while atom A' remains in its ground state. LICET reactions are of the form

$$A_2+A'_1+\hbar\Omega\rightarrow A_1+A'_2 \;. \qquad (2)$$

In this case both atoms change their states as a result of the combined radiative-collisional interaction. A typical level scheme for a LICET reaction is shown in Fig. 1.

Most experiments involving laser-assisted collisions have been carried out with nanosecond laser pulses, whose duration is much larger than the time $\tau_c\simeq 1.0$ ps

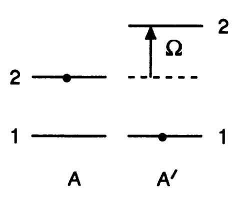

FIG. 1. Level scheme for the LICET reaction $A_2+A'_1+\hbar\Omega\rightarrow A_1+A'_2$. The transition from the initial state $|1\rangle=|21\rangle$ to the final state $|2\rangle=|12\rangle$ proceeds by a virtual intermediate state not shown explicitly in this figure.

of a collision. As a result, the field amplitude can be considered to be constant during a collision. It was proposed by Lee and George [2] that the use of ultrafast pulses, having a duration smaller than or on the order of τ_c, could enhance CARE cross sections. At large atom-field detunings, CARE excitation is produced when the collisional interaction brings the A atom into resonance with the field. In a molecular picture, a crossing occurs at the internuclear separation necessary for this condition to be satisfied. In the time domain, the crossing is traversed twice, on the incoming and outgoing trajectories of the particles. For strong fields, the crossing becomes an anticrossing between dressed atom-field states, with the spacing between the levels equal to the Rabi frequency of the field. The (anti)crossing is then traversed adiabatically. Before the first (anti)crossing, the atoms are in a state that has evolved adiabatically from state $|1\rangle$ of atom A. Following the incoming (anti)crossing the system is in a state that asymptotically goes into state $|2\rangle$ of atom A, but on the outgoing (anti)crossing it returns to a state that asymptotically goes to state $|1\rangle$. The overall transition probability is small, resulting from any nonadiabatic contributions at the (anti)crossings. The idea of Lee and George was that the short pulse will enable the atoms to experience only one (anti)crossing, leading to an increased cross section. These ideas were further developed by Sizer and Raymer [3], who produced experimental evidence for the effect. The experiment has been reanalyzed recently by Miklaszewski and Rebentrost [4].

In CARE, atom-field detunings are sufficiently large to ensure that no excitation occurs without a collision. The situation in LICET is different in that exactly resonant fields can be used since the LICET reaction does not occur unless both collision and radiation fields are present (the LICET transition matrix element depends on the product of radiative and collisional interaction

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strengths). Consequently, it is interesting to look at LICET cross sections near exact resonance. For long pulses, the cross section at the line center (which is shifted by the ac Stark effect) varies as the field intensity in the weak-field limit, and as the field amplitude in the strong-field limit [1]. A preliminary calculation of LICET using ultrafast pulses was given by Payne [5]. He found that the strong-field result is modified significantly if ultrafast pulses are used. Instead of varying as the field amplitude, the LICET excitation profile is approximately field independent over a large range of detunings. Radiative collisions between Rydberg atoms have also been investigated when the reaction occurs during a time interval that is smaller than the collision duration [6,7].

The use of ultrafast pulses in laser-assisted collisions allows for the possibility of using two or more excitation pulses during the *same* collision. In this paper we analyze the LICET cross section when two pulses separated in time by T are incident on an atomic vapor. It is found that Ramsey fringes having spacings of T^{-1} are produced when the LICET cross section is measured as a function of detuning of the incident fields from the overall transition frequency of the LICET reaction. For weak incident fields, the modulation depth and shift of the central Ramsey fringe as a function of (T/τ_c) provide information about the collisional interaction. In strong fields, the modulation depth of the Ramsey fringes increases, but the fringes no longer provide any additional information about the collisional interaction. It should be noted that the Ramsey fringe structure has already been seen in radiative collisions involving Rydberg states [7], but under conditions different from those considered in this work.

The paper is organized as follows: In Sec. II, the general equations for LICET using ultrafast pulses are derived. The LICET cross section in the weak-field limit is calculated in Sec. III, a qualitative discussion of the strong-field limit is given in Sec. IV, and a discussion of the results is presented in Sec. V.

II. THEORY

The energy-level diagram for the two atoms A and A' participating in the LICET reaction is shown in Fig. 1. Initially the atoms are in the composite state $|1\rangle=|21\rangle=|A2\rangle|A'1\rangle$. As a result of the combined action of the incident field and the collision, transition to the final state $|2\rangle=|12\rangle=|A1\rangle|A'2\rangle$ may occur. It is assumed that composite states other than $|1\rangle$ and $|2\rangle$ enter the problem as virtual states only. As a consequence, the state vector for the $A-A'$ system can be written as $|\psi(t)\rangle=a_1(t)|1\rangle+a_2(t)|2\rangle$, where the probability amplitudes a_1 and a_2 satisfy

$$\dot{a}_1=iT(t)a_2-i[\omega_1+S_L(1;t)+S_C(1;t)]a_1\ , \tag{3a}$$

$$\dot{a}_2=iT^*(t)a_1-i[\omega_2+S_L(2;t)+S_C(2;t)]a_2\ , \tag{3b}$$

where $T(t)$ is a matrix element of the effective collisional-radiative operator that couples states $|1\rangle$ and $|2\rangle$, $S_C(i;t)$ is the frequency shift of level i $(i=1,2)$ resulting from the collisional interaction, $S_L(i;t)$ is the frequency shift of level i resulting from the light shift produced by the incident radiation field, and $\omega_i=E_i/\hbar$, where E_i is the energy associated with state $|i\rangle$. General formulas for T, S_C, and S_L can be found in the literature [8], and specific expressions for these quantities are given below.

The electric field of the two incident pulses may be written as

$$\mathbf{E}(\mathbf{R},t)=\frac{1}{2}\sum_{j=1}^{2}\epsilon_j\mathcal{E}_j e^{i\phi_j(t)}e^{i\mathbf{k}_j\cdot\mathbf{R}}e^{-i\Omega t}g(t-t_j)+\text{c.c.}\ , \tag{4}$$

where $g(t)$ is a pulse envelope function centered at $t=0$ having a temporal width of order τ_p. Pulse j has field amplitude $\mathcal{E}_j$, polarization ϵ_j, propagation vector $\mathbf{k}_j$, phase $\phi_j(t)$, and frequency Ω. The time between pulses $T=(t_2-t_1)$ is greater than τ_p but less than or on the order of the collision duration τ_c (see Fig. 2). Furthermore, it is assumed that the pulses are ultrafast; in other words,

$$\tau_p/\tau_c\ll 1\ . \tag{5}$$

At thermal temperatures, τ_c is of order of a picosecond, implying that pulse widths less than or of the order of 100 fs are required for the validity of condition (5). We note in passing that the phase factor $\exp(i\mathbf{k}_j\cdot\mathbf{R})$ at some given atomic site can be arbitrarily set equal to unity since it does not vary significantly during the collision duration τ_c.

When condition (5) holds, the atomic motion can be considered to be frozen during each of the pulses (but not necessarily for the time T between the pulses). Transitions from state $|1\rangle$ to $|2\rangle$ occur at times t_1 and t_2. The interference between the excitation amplitudes at times t_1

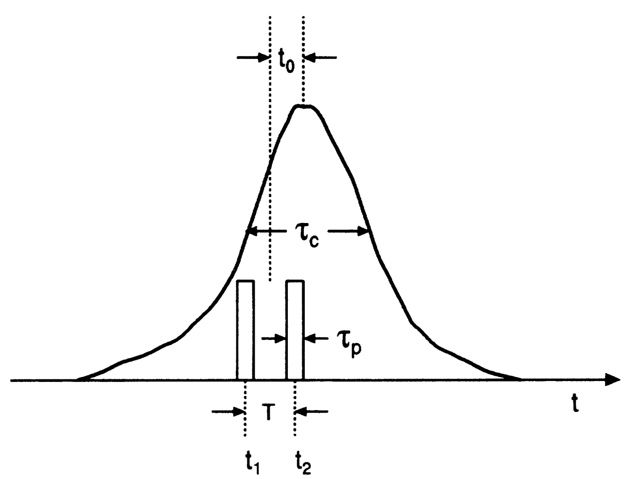

FIG. 2. Schematic picture of the temporal evolution of the laser-assisted collision. The large curve represents the collisional interaction as a function of time for a collision having an impact parameter equal to the Weisskopf radius of pressure broadening theory. The two pulses, represented by square waves in the figure, each have a temporal width $\tau_p\ll\tau_c$. The pulses are separated by T, and the time midway between the pulses is separated from the central time of the collision by t_0.

and t_2 can result in Ramsey fringes.

We now return to Eqs. (3) and adopt specific forms for T, S_C, and S_L [8]. To simplify the discussion, we take $\epsilon_1=\epsilon_2$, $\mathcal{E}_1=\mathcal{E}_2\equiv\mathcal{E}$, and constant phases $\phi_1=\phi_2$. The collisional interaction is assumed to be a dipole-dipole interaction, although the qualitative nature of the results does not depend on this choice. For a dipole-dipole collisional interaction, the coupling strength and collisional shift terms are given by

$$T(t)=2C_3\mathcal{E}[R(t)]^{-3}[g(t-t_1)+g(t-t_2)]\cos(\Omega t) \tag{6a}$$

and

$$S_C(j;t)=C_6(j)/[R(t)]^6 , \tag{6b}$$

respectively, where C_3 and $C_6(j)$ are constants, and $R(t)$ is the $A-A'$ internuclear separation (unless specified otherwise, $j=1,2$). The light shift term can be written as

$$S_L(j;t)=K_j\mathcal{E}^2[g^2(t-t_1)+g^2(t-t_2)] , \tag{6c}$$

where K_j is a constant. In writing Eq. (6c), we neglect a term proportional to $g(t-t_1)g(t-t_2)$, since the incident pulses do not overlap.

Introducing an interaction representation defined by

$$\mathbf{a}_j=\tilde{\mathbf{a}}_j\exp\left\{-i\left[\omega_j t+\int_0^t dt'[S_C(j;t')+S_L(j;t')]\right]\right\} , \tag{7}$$

and dimensionless variables

$$\bar{t}=t/\tau_p , \quad \bar{t}_1=t_1/\tau_p , \quad \bar{t}_2=t_2/\tau_p , \tag{8a}$$

$$\bar{T}=T/\tau_p=\bar{t}_2-\bar{t}_1 , \tag{8b}$$

$$\alpha(\bar{t})=C_3\mathcal{E}[R(\bar{t}\tau_p)]^{-3}\tau_p , \tag{8c}$$

$$F=[C_6(2)-C_6(1)]/(\mathcal{E}^2C_3^2\tau_p) , \tag{8d}$$

$$\mu=(K_2-K_1)\mathcal{E}^2\tau_p , \tag{8e}$$

$$\Delta=[\Omega-(\omega_2-\omega_1)]\tau_p , \tag{8f}$$

one can rewrite Eqs. (3) as

$$\dot{\tilde{\mathbf{a}}}_1=i\sum_{j=1}^{2}\alpha(\bar{t}_j)g[(\bar{t}-\bar{t}_j)\tau_p]\exp\left\{i\Delta\bar{t}-iF\int_0^{\bar{t}}\alpha^2(\bar{t}')d\bar{t}'-i\mu\sum_{j=1}^{2}\int_0^{\bar{t}}g^2[(\bar{t}'-\bar{t}_j)\tau_p]d\bar{t}'\right\}\tilde{a}_2 , \tag{9a}$$

$$\dot{\tilde{\mathbf{a}}}_2=i\sum_{j=1}^{2}\alpha(\bar{t}_j)g[(\bar{t}-\bar{t}_j)\tau_p]\exp\left\{-i\Delta\bar{t}+iF\int_0^{\bar{t}}\alpha^2(\bar{t}')d\bar{t}'+i\mu\sum_{j=1}^{2}\int_0^{\bar{t}}g^2[(\bar{t}'-\bar{t}_j)\tau_p]d\bar{t}'\right\}\tilde{a}_1 . \tag{9b}$$

In writing Eqs. (9), we have used condition (5) to evaluate the coupling terms at $\bar{t}=\bar{t}_j$, have employed the resonance approximation, $|\Delta/\Omega|\ll 1$, and have set "$\cdot$"$=d/d\bar{t}$.

Equations (9a) and (9b) are solved subject to the initial condition

$$\tilde{a}_1(-\infty)=1 , \quad \tilde{a}_2(-\infty)=0 . \tag{9c}$$

The probability amplitude $\tilde{a}_2$ is a function of the collision impact parameter b, relative $A-A'$ speed v, and the (dimensionless) time $\bar{t}_0$ which specifies the interval between the time of closest approach of the collision and the time midway between the two pulses (see Fig. 2). If the central time of the collision is arbitrarily taken equal to zero, then

$$\bar{t}_1=\bar{t}_0-\frac{\bar{T}}{2} , \quad \bar{t}_2=\bar{t}_0+\frac{\bar{T}}{2} . \tag{10}$$

The number of atoms excited per unit volume in a time δt large compared with T and τ_c, but small compared with the pulse repetition rate, is then equal to

$$N(\delta t)=N_AN_{A'}v\int_{-\infty}^{\infty}d\bar{t}_0\int_0^{\infty}2\pi b\,db\,P(\bar{t}_0)|\tilde{a}_2(b,\bar{t}_0;\infty)|^2\delta t , \tag{11}$$

where N_A and $N_{A'}$ are the atom A and A' densities, and $P(\bar{t}_0)=\tau_p/(\delta t)$ is the relative probability for a time interval $\bar{t}_0$. [All times $\bar{t}_0$ in the interval $\delta\bar{t}=\delta t/\tau_p$ are equally likely; however, only times $|\bar{t}_0|\le(\tau_c/\tau_p)$ contribute significantly to the integral.] In principle, result (11) should also be averaged over relative speed v and the spatial distribution of the field [9]. The excitation probability is proportional to a quantity

$$S=v\tau_p\int_{-\infty}^{\infty}d\bar{t}_0\int_0^{\infty}2\pi b\,db\,|\tilde{a}_2(b,\bar{t}_0;\infty)|^2 , \tag{12}$$

which we refer to as the "signal" or the "lineshape."

Before solving Eqs. (9) in various limits, it is useful to introduce a few characteristic phases and radii. During *each* excitation pulse, the probability amplitudes in Eq. (3) acquire a phase shift of order $S_C(t_j)\tau_p$ owing to the collisional shifts and $S_L(t_j)\tau_p$ owing to the light shifts. Moreover, it follows from Eq. (3) that the coupling term $T(t)$ can lead to transition probabilities that vary as $\sin^2$ or $\cos^2[T(t_j)\tau_p]$ when $|T|\gg|S_C|,|S_L|$. *Between* the pulses, there is an additional phase of order $S_C(t_0)T$ produced as a result of the collisional shift term. Finally, it is useful to define the phase $S_C(t=0)\tau_c$ acquired over the entire duration of a collision. This is the phase which would enter for LICET using pulses having temporal widths greater than τ_c.

Each of these phases varies as some inverse power of the internuclear separation R. The LICET transition probability oscillates rapidly as a function of R for $R \le R_{\text{critical}}$, where R_{critical} is a value of R for which any of the phases discussed above is equal to unity. Contributions to the LICET transition probability from the oscillatory region are significantly smaller than those for $R > R_{\text{critical}}$ [1,10,11]; as a consequence, the largest value of R_{critical} associated with the various phases serves as an effective cutoff radius for the problem. Values of these radii are tabulated below.

The radius R_c at which the collisional phase acquired during the pulse duration τ_p is equal to unity is given by

$$(C_6/R_c^6)\tau_p = 1 \ , \tag{13}$$

where

$$C_6 = |C_6(2) - C_6(1)| \ . \tag{14}$$

The radius R_T at which the collisional phase acquired during the interval *between* the two pulses is equal to unity is given by

$$(C_6/R_T^6)T = 1 \ . \tag{15}$$

The radius R_W (often referred to as the Weisskopf radius) at which the collisional phase acquired over the collision interval τ_c is equal to unity is given by

$$(C_6/R_W^6)\tau_c = 1 \ . \tag{16}$$

The collision duration τ_c and radius R_W can be defined such that $R_W = v\tau_c$. Finally, the radius R_e at which the phase acquired from the combined collisional-radiative interaction is equal to unity is given by

$$(|C_3|\mathcal{E}/R_e^3)\tau_p = 1 \ . \tag{17}$$

For weak incident fields (to be defined below), the radius R_c is a cutoff radius for direct excitation by each of the two pulses, while R_T is a cutoff radius for the interference term involving the two pulses. In strong fields ($R_e \gg R_T, R_c$), R_e serves as the cutoff radius for both the direct and interference terms.

The relative contribution of the interference term to the signal must also depend on the ratio (τ_c/T) since, for $(\tau_c/T) \ll 1$, the two pulses cannot occur in the same collision and the interference term must vanish. Thus the signal should depend in some manner on the quantity

$$s = \tau_c/T = R_W/vT \ . \tag{18}$$

III. WEAK-FIELD LIMIT

Perturbation theory is valid provided $|a_2(\infty)|^2$ is much less than unity for the range of impact parameters that contribute to the signal. The major contribution to the integral (12) occurs for $R \ge R_c$, since the integrand oscillates rapidly for $R < R_c$ [1,10,11]. The validity condition for perturbation theory, which follows from Eqs. (13), (17), (8d), and (14), is then

$$R_e \ll R_c \tag{19}$$

or

$$|F| \gg 1 \ , \tag{20}$$

which can always be satisfied for sufficiently small $\mathcal{E}$. In this section, it is also assumed that the light shift term can be neglected, $|\mu| \ll 1$ (for typical atomic parameters, $|\mu F| \approx 1$, implying that $|\mu| \ll 1$ if $|F| \gg 1$).

For the purpose of this calculation, we shall take the pulse envelope function to be given by

$$g(\bar{t}\tau_p) = (1/\sqrt{\pi})\exp(-\bar{t}^2) \ . \tag{21}$$

Setting $\tilde{a}_1(t) = 1$ in Eq. (9b), and solving for $\tilde{a}_2$ using Eq. (21) and condition (5), one finds a transition probability

$$|\tilde{a}_2(\infty)|^2 = \alpha_1^2\exp(-\beta_1^2/2) + \alpha_2^2\exp(-\beta_2^2/2) + 2\,\mathrm{Re}\left\{\alpha_1\alpha_2\exp[-(\beta_1^2+\beta_2^2)/4]\exp\left[-i\Delta\bar{T} + iF\int_{\bar{t}_0-\bar{T}/2}^{\bar{t}_0+\bar{T}/2}\alpha^2(\bar{t}')d\bar{t}'\right]\right\} , \tag{22}$$

where

$$\beta_j = \Delta - F\alpha_j^2 \tag{23}$$

and

$$\alpha_j \equiv \alpha(\bar{t}_j) \ . \tag{24}$$

The first two terms represent the "direct" excitation produced by the individual pulses centered at t_1 and t_2, while the third term is an interference term that can give rise to Ramsey fringes.

To carry out the integrations needed in Eq. (12), it is useful to introduce a cylindrical coordinate system in which $Z = v\tau_p\bar{t}_0$. Then,

$$v\tau_p \int d\bar{t}_0 \int 2\pi b\, db = \int d^3R \ . \tag{25}$$

We consider the direct and interference terms separately.

In the direct terms, one encounters factor of the form

$$\alpha_j = G/R_j^3 \ , \tag{26}$$

where

$$R_j \equiv R(t_j) \tag{27a}$$

and

$$G = C_3\tau_p\mathcal{E} \ . \tag{27b}$$

Assuming straight-line paths for the collisions, one can write

$$(R_{1,2})^2=b^2+(Z\mp Z_1)^2 , \tag{28}$$

where

$$Z_1=vT/2=v\tau_p\bar{T}/2 . \tag{29}$$

Changing variables to $Z'=Z\mp Z_1$, and going over to a spherical coordinate system, one finds that the contribution to the integrated signal (12) from each of the direct terms is the same, and that the total direct signal is given by

$$S_{\text{direct}}=8\pi\int_0^\infty (G/R^3)^2 \times\exp[-(\Delta-FG^2R^{-6})^2/2]R^2dR . \tag{30}$$

Setting $y=FG^2R^{-6}$, one obtains

$$S_{\text{direct}}=S_0 A(\Delta) , \tag{31}$$

where

$$S_0=4\pi G/(3\sqrt{|F|}) \tag{32}$$

and

$$A(\Delta)=\int_0^\infty (y)^{-1/2}\exp[-(y-\epsilon\Delta)^2/2]dy =\sqrt{\pi}e^{-\Delta^2/4}D_{-1/2}(-\epsilon\Delta). \tag{33}$$

The quantity ϵ is defined by

$$\epsilon=F/|F| , \tag{34}$$

and D is a parabolic cylinder function [12]. For $|\Delta|\gg1$ and ϵ negative, the collisional interaction can bring the atoms into resonance with the applied field for negative detunings, but not for positive ones. In this limit, one refers to the line shape for $\Delta\ll-1$ as the quasistatic wing and that for $\Delta\gg1$ as the antistatic wing [1]. For positive ϵ, the quasistatic wing occurs for positive detunings and the antistatic wing for negative ones.

A graph of $A(\Delta)/A(0)$ [$A(0)=2.16$] vs Δ is shown in Fig. 3 (in this, and all subsequent examples, we take $\epsilon=-1$). In the quasistatic wing ($\Delta\ll-1$), it follows

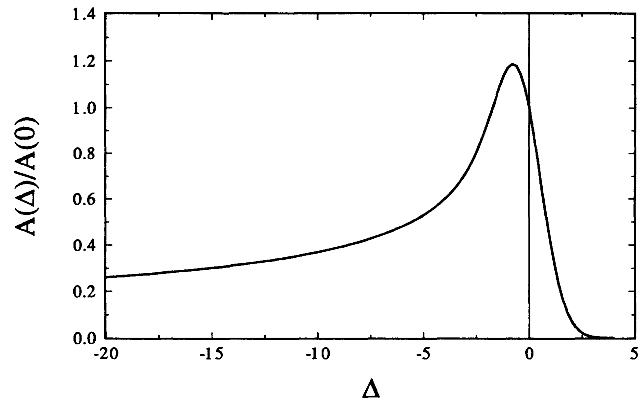

FIG. 3. A graph of the "direct" LICET profile $A(\Delta)$ as a function of dimensionless detuning $\Delta=(\Omega-\omega_{21})\tau_p$. In this and all subsequent graphs, we set $\epsilon=-1$ and normalize such that $A(0)=1$.

from Eq. (33) that $A\sim\sqrt{2\pi/|\Delta|}$, while, in the antistatic wing ($\Delta\gg1$), $A\sim\sqrt{\pi/\Delta}\exp(-\Delta^2/2)$. This marked asymmetry is also found in LICET with long pulses [1]. In contrast to LICET using long pulses, the maximum of the signal does not occur at $\Delta=0$. The maximum occurs at some average collisional shift, a result which can be obtained by differentiating Eq. (33) with respect to Δ. In the impact core of the line ($|\Delta|\ll1$), $A\sim2.16-1.03\Delta$.

We now return to the interference term and write the internuclear separation as

$$R^2(t)=b^2+v^2t^2=b^2+v^2(t-t_0+t_0)^2 =R^2+2Zv(t-t_0)+v^2(t-t_0)^2 , \tag{35}$$

where $R^2=b^2+v^2t_0^2$ and $Z=vt_0=R\cos\theta$ in a spherical coordinate system. With the change of variables $y=FG^2R^{-6}$, $x=R\cos\theta$, one can write the interference term as

$$S_{\text{int}}=S_0B(\Delta,r,\bar{T}) , \tag{36}$$

where

$$B(\Delta,r,\bar{T})=\text{Re}\left\{\exp[-\Delta^2/2-i\Delta\bar{T}]\int_0^\infty dy\int_0^1 dx\, y^{-3/2}(f_+f_-)^{1/2}\exp[-(f_+^2+f_-^2)/4+\epsilon\Delta(f_++f_-)/2] \times\exp\left[i\epsilon y(\bar{T}/2)(r/y)^{1/6}\int_{-(y/r)^{1/6}}^{(y/r)^{1/6}}d\sigma(1+2\sigma x+\sigma^2)^{-3}\right]\right\} , \tag{37}$$

$$f_\pm=y[1\pm2(y/r)^{1/6}x+(y/r)^{1/3}]^{-3} , \tag{38}$$

$$r=|F|G^2/z_1^6=C_6\tau_p/z_1^6=(2R_W/vT)^6(\tau_p/\tau_c)=(2R_T/vT)^6\bar{T}^{-1}=64\bar{T}^{-6}(\tau_c/\tau_p)^5 , \tag{39}$$

and we have used the fact that $R_W=v\tau_c$.

The interference term depends on the two dimensionless parameters $\bar{T}$ and r. There are practical limits on the values of $\bar{T}$ and r. The interference term is clearly a maximum for $r\gg1$, since this corresponds to having both pulses occur at closely separated positions during a collision. On the other hand, one cannot take $\bar{T}$ arbitrarily small, since $\bar{T}>1$ is needed for the observation of Ramsey fringes. For 10-fs pulses, τ_c/τ_p is of order 100. If we want $\bar{T}$ equal to 10, the maximum value of r is of order 6×10^5. Even for somewhat smaller τ_c/τ_p, it is possible to choose $\bar{T}>1$ and still have

$r \gg 1$, allowing for the observation of Ramsey fringes.

Figure 4 shows a plot of the B term for $r=20\,000$ and $\bar{T}=10$ (corresponding to $\tau_c/\tau_p=50$ and $s=R_W/vT=5$), normalized to $A(0)$. The total line shape

$$I=(S_{\rm direct}+S_{\rm int}/S_0)/A(0)=[A(\Delta)+B(\Delta,r,\bar{T})]/A(0) \quad (40)$$

is plotted in Fig. 5. Ramsey fringe structure is clearly seen in these graphs. The central fringe is shifted as a result of the collisional interaction.

The value $r=20\,000$ give results that are approximately equal to those obtained in the asymptotic limit when $r\sim\infty$. The limit $r\sim\infty$ is approached if $(vT/R)\ll 1$ at the cutoff radius R_T [see Eq. (15)] associated with the interference term. Since $r=(2R_T/vT)^6(\bar{T})^{-1}$, values of $r\geq 10^6$ are needed before the asymptotic limit is reached. For such values of r, $(y/r)^6\ll 1$ for all y contributing to the integral (37). In this limit, the interference term can be written as

$$B(\Delta,\infty,\bar{T})={\rm Re}[\exp(-\Delta^2/2-i\Delta\bar{T})\int_0^\infty dy\, y^{-1/2}\exp(-y^2/2+\epsilon\Delta y+i\epsilon y\bar{T})]$$
$$=\sqrt{\pi}{\rm Re}\{\exp(-\Delta^2/2-i\Delta\bar{T})\exp[(\Delta+i\bar{T})^2/4]D_{-1/2}[-\epsilon(\Delta+i\bar{T})]\}\ . \quad (41)$$

For $\bar{T}\gg 1$, it follows from the asymptotic expansion of the parabolic cylinder function [12] that

$$B(\Delta,\infty,\bar{T})\sim\sqrt{\pi}e^{-\Delta^2/2}(\Delta^2+\bar{T}^2)^{-1/4}\times\cos\{\Delta\bar{T}+\tfrac{1}{2}\arg[-\epsilon(\Delta+i\bar{T})]\} \quad (42)$$

which, for $\bar{T}\gg|\Delta|$, reduces to

$$B(\Delta,\infty,\bar{T})\sim\sqrt{\pi}e^{-\Delta^2/2}(\bar{T})^{-1/2}\cos(\Delta\bar{T}-\epsilon\pi/4)\ , \quad (43)$$

with corrections of order $\bar{T}^{-2}$. The maximum amplitude of $B/A(0)$ for $r=\infty$ is 0.260 as compared with a maximum value of 0.254 for $r=20\,000$. The scaling as $(\bar{T})^{-1/2}$ can be easily deduced from the integral expression in Eq. (37). The phase shift of $\pi/4$ as well as the $(\bar{T})^{-1/2}$ dependence is related to the nature of both the LICET coupling strength and the collisional shift term. For a transition matrix element that varies as R^{-m} and a collisional shift term as R^{-n}, the amplitude of the B term (for $r\sim\infty$) varies as $(\Delta^2+T^2)^{-p/2}$ and the phase as $p\{\arg[-\epsilon(\Delta+i\bar{T})]\}$, where $p=1-[(2m-3)/n]$, subject to the constraint that $p>0$.

As τ decreases, the time between pulses approaches and becomes greater than the duration of a collision. As a consequence, one would expect the amplitude of the Ramsey fringes to decrease with decreasing r. This trend is seen in the curves of Fig. 4 drawn for $r=6.4$ and $\bar{T}=10$ (corresponding to $s=R_W/vT=1$ and $\tau_c/\tau_p=10$) and $r=0.2$ and $\bar{T}=10$ (corresponding to $s=R_W/vT=0.5$ and $\tau_c/\tau_p=5$), respectively. An estimate of the scaling for small r can be obtained from Eq. (32) by setting $x=0$ in that equation. For $r\ll 10^{-6}$ (i.e., for $s\ll 0.1$), $g_\pm\sim r$, provided that x is not too close to unity. As a consequence, one sets all the exponential factors in the integrand equal to unity, and finds that the amplitude of the interference term scales as

$$B(0)\sim\int_0^\infty y^{-3/2}[y/[1+(y/r)^{1/3}]dy=(3\pi/8)\sqrt{r}\ . \quad (44)$$

IV. STRONG FIELDS

In this paper, we present only a qualitative picture of the strong-field regime, and defer more quantitative considerations to a future planned paper. The strong-field regime is defined as one in which the cutoff radius R_e associated with the transition coupling term is larger than

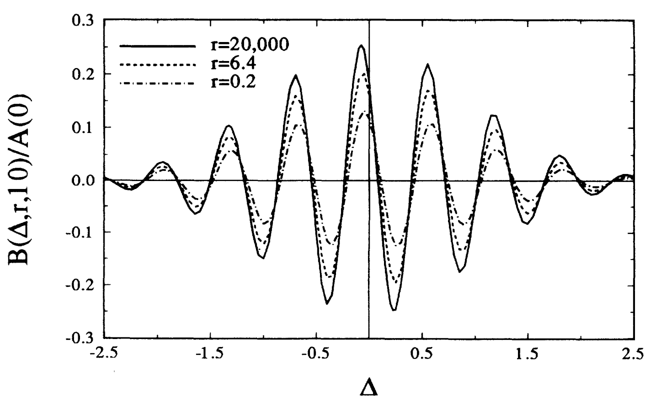

FIG. 4. A graph of the interference term, $B(\Delta,r,\bar{T})/A(0)$, for $\bar{T}=10$ and $r=20\,000$ (solid curve), $r=6.4$ (dashed curve), and $r=0.2$ (dot-dashed curve).

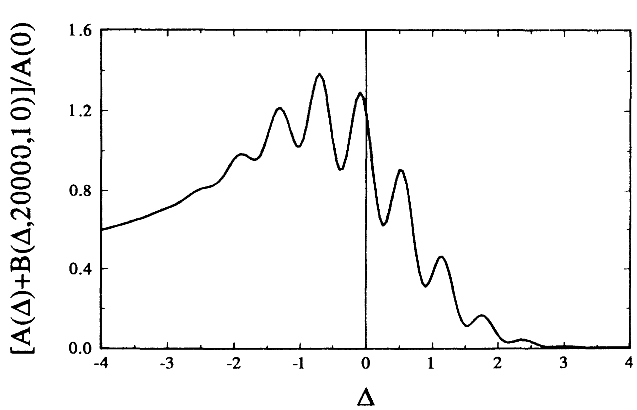

FIG. 5. A graph of the total licet profile, $[A(\Delta)+B(\Delta,r,\bar{T})]/A(0)$, for $r=20\,000$ and $\bar{T}=10$. The Ramsey fringe structure is clearly seen.

R_c, the cutoff radius associated with the collisional shift term. From Eqs. (9), (8c), (8d), and (6b), one sees that the strong-field regime for the direct terms is given by

$$|F|=(R_c/R_e)^6 \ll 1 \ , \tag{45}$$

where R_c and R_e are defined by Eqs. (13) and (17), respectively. When (45) holds, one may neglect the collisional shift that occurs during each excitation pulse.

For the interference term, there are both intermediate- and strong-field regimes. There is a collision-induced phase acquired between the applied pulses that is proportional to $\overline{T}$, and a corresponding cutoff radius R_T [see Eq. (15)]. The intermediate-field regime is defined by $R_T > R_e > R_c$ or

$$|F|\overline{T} \geq 1 \ , \quad |F| < 1 \ . \tag{46}$$

In this limit, the collisional shift acquired during each radiation pulse can be neglected, but the collisional shift acquired *between* the two pulses is not negligible and leads to a decrease in the fringe contrast of the Ramsey fringes just as in the weak-field case. For very strong fields, such that $R_e > R_T > R_c$, or

$$|F|\overline{T} \ll 1 \ , \tag{47}$$

the collisional shift between the pulses can also be ignored and the fringe contrast should approach unity for $v\overline{T}/R_e \ll 1$. In the following discussion, it is assumed that (47) holds. As a consequence the field dependence of the LICET cross section is determined by the effect of a single radiation pulse.

It is perhaps useful to recall that in LICET with long excitation pulses the cross section varies as $\mathcal{E}$ in the strong-field limit. In the long-pulse limit, the phase associated with the transition coupling term varies as $\phi(b)=\kappa\mathcal{E}/b^2$, where b is the collision impact parameter and κ is a constant. Moreover, the Stark shift is *constant* during the collision. In the region of detuning equal to the Stark shift, the major contribution to the LICET cross section comes from those collisions having $b \geq b_0$, where b_0 is the impact parameter defined by $\phi(b_0)=1$; the cross section varies as b_0^2, that is, linearly with $\mathcal{E}$.

The situation for ultrafast pulses is dramatically different. The Stark shift is now a function of time during the excitation process. In the strong-field regime, the Stark shift parameter μ satisfies

$$|\mu| \gg 1 \ . \tag{48}$$

The equations of motion for a single pulse, centered at $t_j=0$, can be written as

$$\dot{\tilde{a}}_1 = i\alpha_0 g(\bar{t}\tau_p)\exp\left[i\Delta\bar{t} - i\mu\int_0^{\bar{t}} g^2(\bar{t}'\tau_p)d\bar{t}'\right]\tilde{a}_2 \ , \tag{49a}$$

$$\dot{\tilde{a}}_2 = i\alpha_0 g(\bar{t}\tau_p)\exp\left\{-i\Delta\bar{t} + i\mu\int_0^{\bar{t}} g^2(\bar{t}'\tau_p)d\bar{t}'\right\}\tilde{a}_1 \ , \tag{49b}$$

where the collisional shift terms have been neglected in the strong-field limit and $\alpha_0 \equiv \alpha(0)$.

We now consider several limiting cases. For a square pulse tuned to the Stark-shifted resonance, the situation is similar to the long-pulse case, and the cross section again varies as $\mathcal{E}$. For a smooth pulse, however, the detuning Δ can equal the Stark shift during the pulse only if

$$|\Delta| < |\mu| g^2(0) \ , \quad \Delta/\mu > 0 \ . \tag{50}$$

Provided conditions (50) holds, it follows from a Landau-Zener treatment at the crossings where the detuning equals the Stark shift that the cross section is almost independent of $\mathcal{E}$ [5,13]. For the detuning

$$\Delta = \mu g^2(0) \ , \tag{51}$$

at which the two crossings coalesce, the uniform approximation gives a cross section that varies as $\mathcal{E}^{1/3}$. For a laser field with a Gaussian spatial profile, there can be a ring, whose radius is determined by Eq. (51), for which the strong-field LICET cross section grows more rapidly than at other points in the beam [14].

V. DISCUSSION

Ramsey fringes appear when a given transition can be driven by two excitation pulses separated in time by T, provided the atomic coherence acquires a phase shift ΔT between the pulses (Δ is an atom-field detuning). Since this is precisely the excitation scheme considered in this paper, the appearance of Ramsey fringes in the LICET profile may not seem surprising. When one considers that the results are averaged over impact parameter and time of closest approach of the atoms, the persistence of the Ramsey fringes is somewhat more mysterious. The qualitative features of the Ramsey fringe pattern can be understood in terms of the various characteristic radii introduced in Sec. II, and the weighting factors which enter the integrated signal (12) and (25).

In the weak-field regime, the weighting factor for the direct terms, obtained from Eqs. (22), (24), and (8c), is proportional to R^2dR/R^6, while that of the interference term is proportional to $R^2dR/[R(t_1)R(t_2)]^3$. Moreover, in the weak-field limit, contributions to the interference term are dominated by collisions having impact parameters $b \geq R_T$, while for the direct terms the range is $b \geq R_c$ (for $|\Delta| \leq 1$). Consider first the limit when $s = R_W/vT \gg 1$, for which $R(t_1) \approx R(t_2) \approx R(t_0) \approx R$. The weighting factors for the direct and interference terms are then approximately equal, leading to a LICET signal proportional to R_c^{-3} for the direct terms and R_T^{-3} for the interference terms. Since $(R_c/R_T) \propto \overline{T}^{1/6}$, the interference to direct term ratio scales as $(R_c/R_T)^3 \propto \overline{T}^{-1/2}$. The collisions with $R > R_T$ that contribute to the interference term result in a shift of the central fringe by an amount of order unity. When T is increased such that $s \leq 1$, one can no longer set $R(t_1) \approx R(t_2)$ and the weighting factor for the interference term must be replaced by $R^2dR/[R(t_1)R(t_2)]^3$. Owing to the fact that the overlap function is small when $T=(t_2-t_1) \gg R_W/v$, the contrast of the Ramsey fringes decreases with increasing T.

In the tail of the quasistatic wing, the major contribution to the LICET profile occurs at a radius $R=(C_6/|\Delta|)^{1/6}<R_c<R_T$. The rapid phase variation of the interference term for such internuclear separations explains the disappearance of the Ramsey fringes in the quasistatic wing, even if $s\gg 1$.

In the intermediate-field regime, the critical radius for the interference term remains equal to R_T, but that for the direct terms is increased to $R_e=(C_3\mathcal{E}/\tau_p)^{1/3}$. As a consequence, the relative contribution of the interference to direct terms scales as $(R_e/R_T)^3 \propto \mathcal{E}(\tau_p/T)^{-1/2}$, which shows that the fringe contrast increases with increasing field amplitude. For very strong fields, all collisional shifts are negligible, and the Ramsey fringe contrast should approach unity.

It is possible to estimate the number of atoms excited per unit volume for each pair of excitation pulses and to estimate the field intensities needed to reach the strong-field regime. As a prototype system, we consider Eu-Sr, which has been studied extensively [1,15]. In all LICET interactions, there is an intermediate state, now shown in Fig. 1, that acts as a virtual state provided the energy of the virtual state is sufficiently detuned from the real energy levels of the system. In the Eu-Sr system this intermediate state has a frequency defect of $\Delta_i \simeq 10^{13}$ s^{-1}. A necessary condition for the two-state approximation to be valid is $|\Delta_i|\tau_p>1$. To satisfy this requirement, we choose $\tau_p=200$ fs. We restrict our discussion to the central part of the excitation profile $|\Delta|\tau_p \le 1$, where the signal is largest.

It is more convenient to write the factors appearing in the coupling term as

$$C_3\mathcal{E}=C_{3'}\chi/\Delta_i \ , \tag{52}$$

where χ is a Rabi frequency associated with the atom-field interaction, and $C_{3'}$ is a constant. For the Eu-Sr system, we can then take [15]

$$\begin{aligned}
&C_6 \simeq (C_{3'})^2/\Delta_i \simeq 4\times 10^{29}\ \text{s}^{-1}\,\text{cm}^{-3}\ ,\\
&\Delta_i \simeq 1.2\times 10^{13}\ \text{s}^{-1}\ ,\\
&v\simeq 5\times 10^4\ \text{cm/s}\ ,\quad \tau_c\simeq 5\ \text{ps}\ ,\quad R_W\simeq 2.5\times 10^{-7}\ \text{cm}\ ,\\
&|\chi|\simeq 10^6\sqrt{I(\text{W/cm}^2)}\text{s}^{-1}\ ,
\end{aligned} \tag{53}$$

where I is the incident laser power density. For the values chosen, $(\tau_c/\tau_p)\simeq 25$, and we are in the large-r limit for $\overline{T}=10$. Note that, if $C_6\simeq (C_{3'})^2/\Delta_i$ and $\mu \simeq |\chi|^2/\Delta_i$, then $|F\mu|\simeq 1$.

With these parameters, the perturbation theory is valid if $|F|<1$, or, equivalently, if

$$|\chi|<(C_6)^{1/2}\Delta_i/(C_3\sqrt{\tau_p})=\sqrt{\Delta_i/\tau_p}\simeq 0.8\times 10^{13}\text{s}^{-1}\ , \tag{54}$$

which corresponds to power densities $I\le 10^{14}$ W/cm^2. This is the threshold power for the intermediate-field regime. The threshold for the very-strong-field regime is given by $|F|\overline{T}=1$, which corresponds to a power density $(\overline{T})^{1/2}$ times that of the intermediate-field threshold. Such power densities are currently available experimentally.

To estimate the number of particles excited per shot, we assume that $N_A=N_{A'}=10^{14}$ cm^{-3} [15] and use Eqs. (11), (12), (32), (33), (36), and (37) to obtain

$$\begin{aligned}
N &\simeq [4\pi N_A N_{A'}(C_{3'})^2|\chi|^2\tau_p^{3/2}/(3\sqrt{C_6}\Delta_i^2)](A+B)\\
&\simeq 10^{-18}|\chi|^2\ .
\end{aligned} \tag{55}$$

For $\chi=10^{13}$ s^{-1} (limit of perturbation theory), a density of 10^8 A' atoms/cm^3 in the interaction volume is excited per shot.

It might be noted in closing that the Ramsey fringes do not probe the short-range part of the interatomic potential since they are produced by collisions having relatively large impact parameters. On the other hand, the quasistatic tail of the direct terms can be used to extract information about the short-range interactions. Additional information can also be obtained by observing the final-state Zeeman coherence induced by the incident polarized fields [1,8,16]. The contrast of the Ramsey fringes would then reflect any depolarization that occurs between the application of the two pulses. It is also possible to envision driving the LICET reaction with a number of phased excitation pulses.

ACKNOWLEDGMENTS

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