Quasistatic wing behavior of collisional-radiative line profiles

A. Bambini
Istituto di Elettronica Quantistica del Consiglio Nazionale delle Ricerche, via Panciatichi 56/30, I50127 Florence, Italy

P. R. Berman
Physics Department, New York University, 4 Washington Place, New York, New York 10003
(Received 10 October 1986)

It is shown that the conventional two-state theory of laser-induced collisional energy transfer (LICET) cannot be expected to provide an adequate description of the quasistatic wing behavior observed in a number of high-resolution LICET experiments. The theory breaks down whenever the detuning parameter Δ of the LICET reaction is comparable to some frequency mismatch $\delta\omega$ between either the initial or final state and a (virtual) intermediate state in the reaction. A simple extension of the conventional two-state theory is presented which leads to good agreement with experiment. For a van der Waals collisional interaction, the quasistatic wing is shown to fall off as $|\Delta|^{-1/2}(\delta\omega+|\Delta|)^{-3/2}$ instead of $|\Delta|^{-1/2}$ predicted by the two-state theory.

INTRODUCTION

Light-induced collisional energy transfer (LICET) has been studied both theoretically[1] and experimentally[1–6] during the past decade. The LICET reaction involves the transfer of excitation energy from one atom to another with the simultaneous absorption or emission of a photon. In the absence of either the collision or the photon, the reaction is rigorously forbidden. The energy-level diagram for a typical LICET reaction,

$$A_i+A'_{i'}+\hbar\Omega\rightarrow A_f+A'_{f'} ,$$

is shown in Fig. 1. Atoms A and A', initially in states i and i', respectively, absorb a photon of frequency Ω while undergoing a collision which takes them to states f and f', respectively. Level $A'_{d'}$ acts as an intermediate virtual level in the reaction (see discussion below).

The LICET profile is obtained by monitoring the $ii'\rightarrow ff'$ cross section as a function of Ω. Experimental LICET line shapes are known to exhibit marked asymmetrices about a central frequency

$$\Omega_0=[(E_f+E_{f'})-(E_i+E_{i'})]/\hbar \tag{1}$$

which represents the transition frequency from initial to

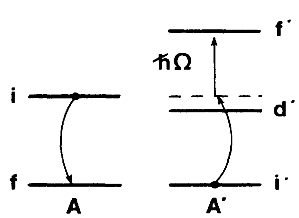

FIG. 1. Energy-level diagram for the LICET reaction $A_i+A'_{i'}+\hbar\Omega\rightarrow A_f+A'_{f'}$. The collision couples initial state $|I\rangle=|ii'\rangle$ to intermediate (virtual) state $|D\rangle=|fd'\rangle$ and the laser field of frequency Ω completes the reaction to final state $|F\rangle=|ff'\rangle$.

final state at large internuclear separations. This asymmetry is well understood in terms of the collision dynamics (Fig. 2). For detunings $\Delta=(\Omega-\Omega_0)<0$, there are internuclear separations for which the transition frequency of the AA' quasimolecule is resonant with the applied field; the instantaneous excitation of the quasimolecule at such internuclear separations leads to a long quasistatic wing in the LICET profile. On the other hand, for $\Delta>0$, no such resonance exists and the so-called antistatic wing falls off sharply once $\Delta\tau_c>1$, where τ_c is the collision duration.

Although the qualitative structure of the LICET line shape is fairly well understood, the quantitative dependence of the quasistatic wing for $|\Delta|\tau_c\gg1$ has remained somewhat of a puzzle. Theories of LICET based on a van der Waals collisional interaction lead to a prediction of a $|\Delta|^{-0.5}$ falloff for the quasistatic wing. Experimentally, one has observed a $|\Delta|^{-\alpha}$ dependence, with $\alpha=0.85$ and 0.80 for a Eu-Sr LICET reaction,[3,5]

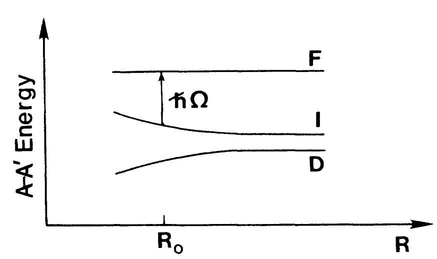

FIG. 2. Energy of the AA' quasimolecule (in arbitrary units) as a function of AA' internuclear separation R. The labels F, I, and D label the *asymptotic* states in the product basis, $I=ii'$, $D=fd'$, $F=ff'$. The collision is adiabatic in the sense that the quasimolecular state $\tilde{D}$ is not populated during the LICET collision and the transition occurs from quasimolecular state $\tilde{I}$ to $\tilde{F}$. For the field frequency shown, an instantaneous resonance for the $\tilde{I}$-$\tilde{F}$ transition in the quasimolecule occurs at internuclear separation $R=R_0$.

$\alpha=0.8$ for Na-Ca (Ref. 6), and $\alpha=0.5$ for Sr-Li.[4] It is difficult to explain the $\alpha=0.80$ and 0.85 results on the basis of any reasonable interatomic potential within the framework of the conventional theory. In this communication, we present a simple extension of the conventional theory which may offer a unified explanation of the experimental data. The explanation is based on an improved method for including the effects of virtual level d' in the calculation.

REVIEW OF CONVENTIONAL THEORY

In order to understand our modification of the conventional theory, we first review several features and assumptions of the simplest form of that theory. (1) Atoms A and A' are assumed to follow classical trajectories with an internuclear separation $R(t)$. (2) The collision occurs on a time scale that is short compared with the laser pulse duration; consequently, the laser-field amplitude can be taken as constant during the collision. (3) The laser-field frequency Ω is sufficiently close to Ω_0 so that terms of order $|\Omega-\Omega_0|/(\Omega+\Omega_0)$ may be neglected (rotating-wave approximation). (4) Changes in the atom's center-of-mass energy resulting from the energy mismatch between initial and final states (including the photon energy) are ignored. (5) All states other than the initial and final ones enter the calculation as virtual states only—their population *during* and after the collision is taken to be negligibly small. The last approximation enables one to reduce the conventional LICET calculation to an effective two-level problem.

Within the confines of the above approximations it is relatively easy[1,7] to derive equations of motion for the initial- and final-state probability amplitudes. These equations contain: (1) a level-shifting or light-shift term produced by the laser field, (2) a level-shifting term produced by the collisional interaction, and (3) a transition term, depending on *both* the collisional interaction and the laser field—this is the term responsible for the LICET reaction. Each of these terms contains an infinite sum over the virtual excitations of the atoms produced by the collision and/or the field. To simplify the discussion, we adopt the following two additional assumptions: (1) The light shifts which, in principle, can be included by a renormalization of the atomic energy levels, are neglected. In any event, these shifts are small for the experiments to be discussed. (2) Owing to a near-resonant enhancement

$$[(E_i+E_{i'})\simeq(E_f+E_{d'})] ,$$

the only virtual excitation that need be considered for the collisional shift and LICET transition terms is that involving state $|fd'\rangle$ of the quasimolecule AA'. This assumption is not critical to the present discussion, but simplifies the presentation—the contributions from other virtual excitations may be easily incorporated into the calculation, if desired. For the actual experiments under discussion, a single intermediate state provides the dominant contribution to the collisional shift and LICET transition operators.[8]

With the above assumptions, there are just three states of the product A-A' basis which enter the calculation, namely

$$|I\rangle=|i\rangle|i'\rangle,\ |D\rangle=|f\rangle|d'\rangle,\ |F\rangle=|f\rangle|f'\rangle .$$

The collisional interaction $V_c[R(t)]$ is responsible for a virtual excitation of state $|D\rangle$ from state $|I\rangle$ and the field completes the LICET reaction by coupling state $|D\rangle$ to state $|F\rangle$. The corresponding equations of motion for probability amplitudes $a_M(t)$ $(M=I,D,F)$ in the interaction representation are

$$\dot a_I=-iU_c e^{i\omega_{ID}t}a_D , \tag{2a}$$

$$\dot a_D=-iU_c e^{-i\omega_{ID}t}a_I+i\chi e^{+i(\Omega-\omega_{FD})t}a_F , \tag{2b}$$

$$\dot a_F=-i\chi e^{-i(\Omega-\omega_{FD})t}a_D , \tag{2c}$$

where

$$\omega_{MN}=\omega_M-\omega_N , \tag{3a}$$

$$\omega_I=(E_i+E_{i'})/\hbar,\ \omega_D=(E_f+E_{d'})/\hbar ,\quad \omega_F=(E_f+E_{f'})/\hbar , \tag{3b}$$

$$U_c(t)=V_c(t)/\hbar , \tag{4}$$

and $\chi=\mu_{e'f'}\mathcal{E}/2\hbar$ [$\mathcal{E}$ is the (constant) laser-field amplitude during the collision, $\mu_{e'f'}$ is the $e'f'$ dipole moment matrix element].

In the conventional two-state theory, it is now assumed that intermediate state D enters the problem as a virtual state only, i.e., that

$$|a_D(t)|\ll 1 \tag{5}$$

for all t. As will be shown below, a sufficient condition for inequality (5) to hold is that the frequency mismatch ω_{ID} be much larger than all other relevant frequency parameters in the problem. In that limit, one can calculate $a_D(t)$ to lowest order by integrating Eq. (2b) by parts. When the lead terms of this integration by parts are substituted into Eqs. (2a) and (2c), one obtains

$$\dot a_I=-i(U_c^2/\omega_{ID})a_I+i[\chi U_c/(\omega_{ID}-\Delta)]e^{i\Delta t}a_F , \tag{6a}$$

$$\dot a_F=i(\chi U_c/\omega_{ID})e^{-i\Delta t}a_I , \tag{6b}$$

where the detuning Δ is defined by

$$\Delta=\Omega-\omega_{FI} . \tag{7}$$

[A light-shift term, proportional to $\chi^2/(\omega_{ID}-\Delta)$ has been dropped from (6b).] The collisional-shift term (proportional to $[U_c(R)]^2$) and the LICET transition term (proportional to $|\chi U_c(R)|$) are evident in these equations. These equations are solved for $|a_F(\infty)|^2$, subject to the initial conditions

$$a_I(-\infty)=1;\ a_F(-\infty)=0 . \tag{8}$$

The transition probability $|a_F(\infty)|^2$, averaged over collision-impact parameter and laser-field strength, gives the LICET cross section as a function of detuning Δ. The cross section displays the general qualitative features discussed in the Introduction.

The validity of Eqs. (6) rests on inequality (5) [$|a_D(t)|\ll 1$], which must hold for times during and after the collision. If, as in most LICET experiments, the condition

$$\omega_{ID}\tau_c \gg 1 \tag{9}$$

is satisfied, then, owing to energy-time uncertainty considerations, the value of $|a_D(t)|$ following the collision is of order $\exp(-\omega_{ID}\tau_c) \ll 1$. Condition (9) is necessary for the validity of Eqs. (6), but not sufficient. For times *during* the collision when $U_c(t) \neq 0$, it is possible to integrate the first term of Eq. (2b) by parts using the fact that $\omega_{ID}\tau_c \gg 1$ to show that the condition $|a_D(t)| \ll 1$ necessary for the validity of the effective two-state problem can be satisfied only if

$$|U_c(R)/\omega_{ID}| \ll 1 ; \tag{10}$$

that is, provided the collisional coupling strength is much less than the frequency mismatch. In the quasistatic wing ($|\Delta|\tau_c \gg 1$), the R to use in Eq. (10) is just that internuclear separation for which the quasimolecular energy levels are resonant with the applied field (Fig. 2), namely when $U_c(R) \simeq \Delta$. In that limit, inequality (10) becomes

$$|\Delta|/\omega_{ID} \ll 1 . \tag{11}$$

This condition is *not* satisfied in many LICET experiments [e.g., for Eu-Sr, $\omega_{ID}/(2\pi c) = 63\ \text{cm}^{-1}$ while values $|\Delta/2\pi c|$ as large as 50 cm^{-1} were recorded[3]]. Consequently, the use of Eqs. (6) is not justified in the analysis of such problems.

[An additional condition for the validity of Eqs. (6) is found by integrating the second term of Eq. (2b) by parts assuming $\omega_{ID}\tau_c \gg 1$. The condition one obtains in this manner, $|\chi/(\Omega-\omega_{FD})| = |\chi/(\omega_{ID}-\Delta)| \ll 1$, is normally satisfied for the field strengths and detunings of typical LICET experiments (note that the quasistatic wing corresponds to detunings $-1 \lesssim \Delta/\omega_{ID} < 0$ and the antistatic wing to detunings $0 < \Delta/\omega_{ID} \ll 1$). Thus, the breakdown of the two-state approximation is usually associated with a violation of inequality (11).]

EXTENSION OF THE THEORY

When condition (11) no longer holds, it is necessary to return to Eqs. (2). We shall be content with a solution to these equations that is perturbative with respect to the laser-field amplitude. In the quasistatic wing, ($|\Delta|\tau_c \gg 1$), a perturbation solution is sufficiently accurate at typical experimental laser powers. To first order in χ, the final-state amplitude following the LICET reaction is obtained from (2c) as

$$a_F(\infty) = i\chi \int_{-\infty}^{\infty} e^{-i(\Omega-\omega_{FD})t} a_D(t)\,dt , \tag{12}$$

where $a_D(t)$ is the solution of Eqs. (2a) and (2b) to zeroth order in χ; i.e., a solution of

$$\dot{a}_I = -iU_c e^{i\omega_{ID}t} a_D , \tag{13a}$$

$$\dot{a}_D = -iU_c e^{-i\omega_{ID}t} a_I , \tag{13b}$$

subject to the initial conditions $a_I(-\infty) = 1$, $a_D(-\infty) = 0$. Note that $a_F(\infty)$ is just the Fourier transition of a_D at frequency defect $(\Omega - \omega_{FD})$.

We are interested in the solution of Eqs. (13) in the limit that $\omega_{ID}\tau_c \gg 1$; that is in the limit that state $|D\rangle$ is *not* populated following the collision $a_D(\infty) = 0$. (This is the appropriate limit for the cases of experimental interest[3–6] where $\omega_{ID}\tau_c$ ranges from 10 to 45.) If $\omega_{ID}\tau_c \gg 1$, an approximate solution to Eqs. (13) can be generated as follows: First, one sets

$$a_I(t) = \alpha_1(t), \quad a_D(t) = \alpha_2(t) e^{-i\omega_{ID}t} \tag{14}$$

and uses Eqs. (13) to write

$$\dot{\boldsymbol{\alpha}} = iH\boldsymbol{\alpha}, \quad \boldsymbol{\alpha} = \begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix}, \quad \mathbf{H} = \begin{bmatrix} 0 & -U_c \\ -U_c & \omega_{ID} \end{bmatrix} . \tag{15}$$

Second, a transformation $\mathbf{b} = T(t)\boldsymbol{\alpha}$ is introduced in which $T^{-1}(t)H(t)T(t)$ is diagonal. A matrix T that accomplishes this transformation is

$$T = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \tag{16}$$

provided that[9]

$$\cos\theta = \frac{1}{\sqrt{2}} \left[1 + \frac{\omega_{ID}}{\omega_{12}} \right]^{1/2}, \quad \sin\theta = \frac{1}{\sqrt{2}} \left[1 - \frac{\omega_{ID}}{\omega_{12}} \right]^{1/2} \tag{17}$$

where

$$\omega_{12} = (\omega_{ID}^2 + 4U_c^2)^{1/2} . \tag{18}$$

Third, the transformation $\mathbf{b} = T\boldsymbol{\alpha}$ is substituted into (15) to obtain

$$\dot{\mathbf{b}} = -i \begin{bmatrix} \epsilon_1 & -i\dot{\theta} \\ i\dot{\theta} & \epsilon_2 \end{bmatrix} \mathbf{b} ,$$
$$b_1(-\infty) = 1, \quad b_2(-\infty) = 0; \ \epsilon_{1,2} = \tfrac{1}{2}(-\omega_{ID} \pm \omega_{12}) . \tag{19}$$

The transformation from Eq. (15) to Eq. (19) corresponds physically to a transformation from a separated atom to a quasimolecular basis. The quasimolecular energy levels associated with this transformation are shown in Fig. 2 as a function of internuclear separation, where quasimolecular levels $\tilde{I}$ and $\tilde{D}$ correspond to states 1 and 2, respectively, in the b basis, and where the frequency separation of quasimolecular states $\tilde{I}$ and $\tilde{D}$ is equal to $\epsilon_1 - \epsilon_2 = \omega_{12}$. The initial condition $b_1(-\infty) = 1$ corresponds to the atoms entering the collision in state $\tilde{I}$. If the $\dot{\theta}$ terms in Eq. (19) can be neglected, the atoms adiabatically follow quasimolecular level $\tilde{I}$ before the interaction with the radiation field completes the LICET reaction to state $\tilde{F}$ (Fig. 2). It is an easy matter to show that the adiabatic approximation [neglect of the $\dot{\theta}$ terms in Eq. (19)] is valid provided that $\omega_{12}\tau_c \gg 1$. To prove this explicitly, one solves Eq. (19) to first order in $\dot{\theta}$ and uses an integration by parts to show that the transition amplitude produced by the $\dot{\theta}$ terms is of order $(\omega_{12}\tau_c)^{-1} \ll 1$. This condition simply corresponds to the fact that the frequency components contained in the nonadiabatic $\dot{\theta}$ coupling terms, which are of order τ_c^{-1}, are insufficient to cause transitions between the quasimolecular levels $\tilde{I}$ and $\tilde{D}$ which are separated in frequency by ω_{12}. Once the $\dot{\theta}$ terms are dropped, Eq. (19) is easily solved and the inverse transformation $\boldsymbol{\alpha}=T^{-1}\mathbf{b}$ and Eq. (14) are used to obtain

$$a_D(t)=-\sin\theta e^{-i\omega_{ID}t}\exp\left[\tfrac{1}{2}i\int_{-\infty}^{t}[\omega_{ID}-\omega_{12}(t')]dt'\right] . \tag{20}$$

When this approximate solution is substituted into Eq. (12), one finds the LICET transition probability

$$|a_F(\infty)|^2 = \left|\chi\int_{-\infty}^{\infty}e^{-i\Delta t}\sin[\theta(t)] \times\exp\left[\tfrac{1}{2}i\int_{-\infty}^{t}[\omega_{ID}-\omega_{12}(t')]dt'\right]dt\right|^2 \tag{21}$$

where Eq. (7) has been used.

In the quasistatic wing, the major contribution to the integral occurs at those times (or internuclear separations) for which the AA' quasimolecule is resonant with the field. These separations are nothing more than the points of stationary phase of the integrand in (21). There will be two points of stationary phase ($\pm t_s$) provided that the impact parameter b of the collision is less than a critical impact parameter b_0 (to be defined below). For collisions with impact parameters $b<b_0$, the integral (21) evaluated by the method of stationary phase yields

$$|a_F(\infty)|^2=|\chi|^2\pi(-\Delta)|U_c(t_s)\dot{U}_c(t_s)|^{-1} \times|e^{i[\phi(t_s)+\phi/4]}+e^{i[\phi(-t_s)-\pi/4]}|^2 , \tag{22}$$

where t_s is defined as the positive solution to

$$\omega_{ID}-\omega_{12}(t_s)=\Delta<0 \tag{23}$$

and

$$\phi(t)=-\Delta t+\tfrac{1}{2}\int_{-\infty}^{t}[\omega_{ID}-\omega_{12}(t')]dt' . \tag{24}$$

This is as far as we can go without assuming an explicit form for $U_c(R)$.

A reasonable choice for $U_c(R)$ is a van der Waals interaction

$$U_c(R)=-C/R^3,\quad C>0 . \tag{25}$$

With this choice and the additional assumption that the collision trajectory is linear [$R^2=(b^2+v^2t^2)$, where v is the AA' relative speed], the stationary-phase condition (23) becomes

$$C^2/(b^2+v^2t_s^2)^3=-\Delta(\omega_{ID}-\Delta) \tag{26}$$

which can be satisfied by impact parameters b less than b_0 defined by

$$b_0=[-C^2/\Delta(\omega_{ID}-\Delta)]^{1/6} . \tag{27}$$

Combining Eqs. (22)—(27), one finds

$$|a_F(\infty)|^2=\tfrac{1}{3}|\chi|^2\pi b_0[v^2(1-b^2/b_0^2)]^{-1/2}(\omega_{ID}-\Delta)^{-1} \times|e^{i[\phi(t_s)+\pi/4]}+e^{i[\phi(-t_s)-\pi/4]}|^2 , \tag{28}$$

valid for $|\Delta|\tau_c\gg1$, $\Delta<0$, and $b<b_0$.

If Eq. (28) is multiplied by $2\pi b\,db$ and integrated from 0 to b_0, one obtains the LICET cross section

$$\sigma=\frac{4}{3}\,\frac{\pi^2|\chi|^2C}{v(-\Delta)^{1/2}(\omega_{ID}-\Delta)^{3/2}} . \tag{29}$$

In deriving (29), the contribution from the oscillatory cross terms varying as

$$\exp\pm\{i[\phi(t_s)-\phi(-t_s)]\}$$

was neglected. For $\omega_{ID}\gg|\Delta|$, $\sigma\sim|\Delta|^{-1/2}$, and one regains the conventional result. If $\omega_{ID}\simeq-\Delta$, the falloff with Δ is more rapid than $|\Delta|^{-0.5}$.

DISCUSSION

We have shown that the conventional two-state theory for the quasistatic wing of the LICET profile breaks down if the overall detuning $|\Delta|$ is comparable to the frequency mismatch between initial and intermediate states ω_{ID}. A simple extension of the theory was given for the detuning dependence of the quasistatic wing based on the following assumptions: (1) The laser field can be treated perturbatively. (2) There is only one intermediate state $|D\rangle=|fd'\rangle$ which need be considered, owing to a near-resonant enhancement of the LICET reaction. (3) The intermediate state may be populated during the collision but *not* following it, i.e., $\omega_{ID}\tau_c\gg1$ (τ_c is the collision duration). With these assumptions, it was shown that the detuning dependence of the quasistatic wing for a van der Waals collision interaction is $(\omega_{ID}-\Delta)^{-3/2}(-\Delta)^{-1/2}$ instead of $(-\Delta)^{-1/2}$ predicted by the two-state theory.

The question that remains is whether or not this theory can explain experimental LICET profiles. We consider three cases where high-resolution LICET profiles were reported:

(1) Eu-Sr:[3,5] The frequency mismatch ω_{ID} (in cm^{-1}) is 63 cm^{-1} and a detuning range to $\Delta=-55$ cm^{-1} was recorded. Since $|\Delta|\simeq\omega_{ID}$, the two-state theory cannot be expected to remain valid. The detuning dependence predicted by Eq. (29) for the range $10\ \text{cm}^{-1}<|\Delta|<50\ \text{cm}^{-1}$ is plotted in Fig. 3 along with the $(-\Delta)^{-0.85}$ dependence observed experimentally.[3,5] The results are in relatively good agreement. In a related problem of collisionally aided excitation of Eu($J=\frac{9}{2}$) (with Sr perturbers), Niemax observed a crossover from $(-\Delta)^{-1.5}$ to $(-\Delta)^{-2}$ dependence at $\Delta\simeq-47$ cm^{-1}.[10] The modified theory for collisionally aided excitation analogous to that for LICET leads to a $(-\Delta)^{-1.5}(\omega_{ID}-\Delta)^{-0.5}$ prediction, consistent with Niemax's result.

(2) Na-Ca:[6] The mismatch is $\omega_{ID}=-94$ cm^{-1}, -111 cm^{-1} (two states contribute) and detunings to $\Delta=60$ cm^{-1} were monitored.[11] The experimental dependence observed was $\Delta^{-0.8}$, but some assumptions on the additivity of the $3P_{1/2}$ and $3P_{3/2}$ initial states was needed to reach this conclusion. Comparison with theory is shown in Fig. 3 for $\omega_{ID}=-94$ cm^{-1} (the correspond-

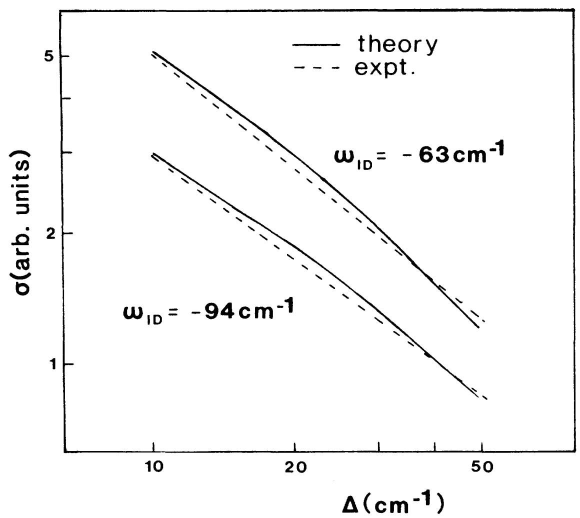

FIG. 3. Graphs of LICET cross section σ (in arbitrary units) as a function of detuning Δ (in cm^{-1}) for energy defects $\omega_{ID}=-63$ cm^{-1} (Eu-Sr) and $\omega_{ID}=-94$ cm^{-1} (Sr-Ca). The solid curves represent the theoretical profiles. The dashed curves give the experimental $\Delta^{-0.85}$ (Eu-Sr) and $\Delta^{-0.8}$ (Sr-Ca) profiles. The point at $\Delta=10$ cm^{-1} is chosen to normalize the theoretical and experimental curves.

ing curves drawn for $\omega_{ID}=-111$ cm^{-1} do not differ appreciably from those shown for $\omega_{ID}=-94$ cm^{-1}).

(3) Sr-Li:[4] The mismatch is $\omega_{ID}\simeq-21$ cm^{-1} and detunings to $\Delta=70$ cm^{-1} were recorded.[11] One would have expected a crossover from $\Delta^{-0.5}$ to Δ^{-2} dependence at $\Delta\simeq 20$ cm^{-1}, but no such effect was reported. The experimental curve was consistent with the $\Delta^{-0.5}$ prediction of the two-state theory, but not with our modified theory. Recently, this experiment has been repeated at a lower temperature and with improved detector sensitivity.[12] The new data show both a $\Delta^{-0.5}$ dependence for $\Delta \lesssim 20$ cm^{-1} and a $\Delta^{-2.0}$ dependence for $\Delta \gtrsim 20$ cm^{-1}. Thus, the new data are in very good agreement with our theory, assuming a van der Waals collisional interaction.

In summary, we have shown that the conventional two-state LICET theory fails whenever detunings are comparable to a frequency mismatch of an intermediate virtual state ($|\Delta|\simeq\omega_{ID}$). Since most LICET experiments have been carried out in this detuning range, it is not surprising that the LICET profiles do not agree with the conventional theory. We have provided a simple extension of the conventional theory which gives much better agreement with experiment.

ACKNOWLEDGMENTS

We would like to thank Professor E. J. Robinson for helpful comments. The research of P. R. B. is supported by the U. S. Office of Naval Research. We also wish to thank Professor Toschek for communication of the results of F. Dorsch (Ref. 12) prior to publication.

[1]For review of this subject area containing additional references, see P. R. Berman and E. J. Robinson in *Photon-Assisted Collisions and Related Topics,* edited by N. K. Rahman and C. Guidotti (Harwood, Chur, Switzerland, 1982), pp. 15—33; S. I. Yakovlenko, Sov. J. Quantum Electron. **8**, 151 (1978); M. G. Payne, V. E. Anderson, and J. E. Turner, Phys. Rev. A **20**, 1032 (1979). In a recent article [H. Yagisawa and K. Yagisawa, Phys. Rev. A **29**, 2479 (1984)], a calculation was presented including the effects of a third state, but the approach was different than that considered in this work.

[2]The first experiments in this area were carried out by Harris *et al.*, For a review of this work, see S. E. Harris, J. F. Young, W. R. Green, R. W. Falcone, J. Lukasik, J. C. White, J. R. Willison, M. D. Wright, and G. A. Zdasiuk, in *Laser Spectroscopy IV,* edited by H. Walther and K. W. Rothe (Springer-Verlag, Berlin, 1979), pp. 349—359.

[3]C. Bréchignac, Ph. Cahuzac, and P. E. Toschek, Phys. Rev. A **21**, 1969 (1980).

[4]D. Z. Zhang, B. Nikolaus, and P. E. Toschek, Appl. Phys. B **28**, 195 (1982).

[5]A. Débarre, J. Phys. B **15**, 1693 (1982).

[6]A. Débarre, J. Phys. B **16**, 431 (1983).

[7]P. R. Berman, Phys. Rev. A **22**, 1838, (1980); **22**, 1848 (1980).

[8]It is assumed that the energy mismatch for state $|id'\rangle$ is sufficiently large that it need not be considered in the context of this calculation.

[9]We assume $U(t)<0$. For $U(t)>0$, a negative sign for $\sin\theta$ should be taken.

[10]K. Niemax, Phys. Rev. Lett. **55**, 56 (1985).

[11]The pathway for this LICET reaction is different than that shown in Fig. 1. It involves the virtual excitation of state $|id'\rangle$ (which serves as the dominant intermediate state) by the field, followed by the collisional excitation of state $|ff'\rangle$) from $|id'\rangle$. The equations describing the process differ somewhat from Eqs. (2) of the text, but, in the perturbation theory limit, the final-state probability $|a_F(\infty)|^2$ is still given by Eq. (21), with ω_{ID} replaced by $\omega_{FD'}[|D'\rangle=|id'\rangle]$.

[12]F. Dorsch, diploma thesis, University of Hamburg, 1986 (unpublished).