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THREE-STATE MODEL FOR LASER-ASSISTED COLLISIONS

P. R. Berman

Physics Department, New York University
4 Washington Place, New York, NY 10003 USA

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I. Introduction

A laser-assisted collision (LAC) is one involving a combined collisional-radiative interaction. A typical laser-assisted collision can be written as a reaction of the form

$$A_i + \hbar\Omega \rightarrow A_f \quad (1)$$

where $|I\rangle$ and $|F\rangle$ are composite initial and final states, respectively, of atoms A and A' which are undergoing the collision, and Ω is the frequency of the laser field which produces the transition from initial to final state. The eigenkets $|I\rangle$ and $|F\rangle$ may be expressed in terms of the individual atomic-state eigenkets as $|I\rangle = |i\rangle|i'\rangle$, $|F\rangle = |f\rangle|f'\rangle$, where unprimed states refer to atom A and primed states refer to atom A'. Laser-assisted collisions have been classified into two broad categories. First, there are the so-called "optical collisions" [1] (or Collisionally-Aided Radiative Excitation (CARE) [2]) involving reactions of the form

$$A_i + A'_{i'} + \hbar\Omega \rightarrow A_i + A'_{f'} \quad (2)$$

in which the state of atom A is unchanged. The transition from state i' to f' in atom A' is accompanied by the absorption of a photon of frequency Ω which is assumed to be non-resonant with the $i'-f'$ transition frequency. Consequently, the role of the collision is to provide or extract translational energy to compensate for the energy defect between the photon and transition frequencies. Second, there are the so-called "radiative collisions" [3] (or Laser-Induced Collisional Excitation Transfer (LICET) [4] or Radiatively-Aided Inelastic Collisions (RAIC) [2]) involving reactions of the form

$$A_i + A'_{i'} + \hbar\Omega \rightarrow A_f + A'_{f'} \quad (3)$$

in which both atoms change their internal state. Any difference between the photon and (composite) initial to final state transition frequency can

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again be compensated by a corresponding change in the translational energy of the colliding atoms. Reviews of both CARE and LICET can be found in the literature [5].

In a typical LAC experiment [6,7], atoms A and A' are contained in a cell or in a heat pipe oven. Pulsed laser radiation is used both to produce the initial state $|I\rangle$ (in LICET experiments) and also to provide the photons of frequency Ω which drive the laser-assisted collision. The LAC cross section is measured as a function of detuning

$$\Delta = \Omega - \omega_{FI} = \Omega - (E_F - E_I)/\hbar \quad (4)$$

of the applied laser field frequency from the over-all transition frequency ω_{FI} . The LAC excitation profile which emerges from such studies, as shown in Fig. 1, exhibits a marked asymmetry about $\Delta\tau_c = 0$ ($\tau_c =$ collision

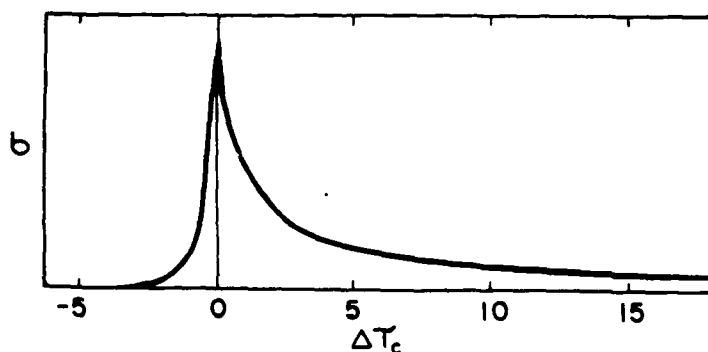


Fig. 1. Typical laser-assisted collision profile [cross section σ (arbitrary units) as a function of dimensionless detuning $|\Delta\tau_c|$ showing a long quasistatic tail for $\Delta > 0$.

duration). The long tail occurring for positive $\Delta\tau_c$ in Fig. 1 is referred to as the quasistatic wing, while that part of the profile which drops off rapidly for negative $\Delta\tau_c$ is referred to as the antistatic wing.

In general there has been both very good qualitative and very good quantitative agreement between theoretical and experimental LAC profiles. The line shape asymmetry is explained in terms of quasimolecular resonances which occur for one sign of the detuning but not the other. The good agreement between theory and experiment encouraged several groups to examine LAC in more detail. As a result of this work [8,9], theoretical

and experimental LAC cross sections were obtained for final magnetic-state polarization as well as final-state total population. By studying both the magnetic-state and total LAC cross sections, one can obtain rather detailed information about the A-A' interatomic potential [8]. In this paper, I will concentrate, for the most part, on a discussion of total rather than magnetic-state LAC cross sections.

It would appear that there is not much left to discuss, given the relatively good agreement between theory and experiment. While the agreement between theory and experiment is good, it is by no means perfect. In particular, there has been a persistent and systematic disagreement between theoretical predictions and experimental observations for the fall-off with Δr_c of the quasistatic wing of LICET profiles. Theory [5] predicts a $|\Delta|^{-0.5}$ fall-off for a dipole-dipole collisional interaction, while experiment [10-12] often reveals a dependence which varies more like $|\Delta|^{-0.8}$. Even if one modifies the theory to allow for alternative collisional interactions, there is no way to consistently account for this discrepancy within the context of the conventional theory.

It is the purpose of this report to review a simple generalization of the conventional theory [13,14] which leads to much better agreement between theory and experiment in the quasistatic wing of the LICET profiles. The results also can be applied to the analysis of a recent CARE experiment carried out by Niemax [15]. The basic theory of LAC using a quasimolecular picture is presented in Sec. II. The LAC cross section in the quasistatic wing is expressed in terms of a number of parameters which are evaluated in Sec. III. The parameters are evaluated using a modified version of the conventional theory which allows one to take into account the contributions from a nearly resonant intermediate state. This is the three state model referred to in the title of this paper. A comparison between theory and experiment is given in Sec. IV.

II. Review of CARE and LICET

Both the CARE and LICET reactions are represented schematically by Eq.(1), in which a single photon of frequency Ω from a field having amplitude E_0 is absorbed during a collision, taking the atoms A and A' from some initial composite state $|I\rangle = |ii'\rangle$ to a final composite state $|F\rangle = |ff'\rangle$.



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To simplify the discussion somewhat, the following assumptions or approximations will be made throughout this paper; (1) LICET and CARE cross sections are calculated to lowest non-vanishing order (E_0^2) of the applied radiation field. (2) The field frequency is nearly equal to the composite frequency ω_{FI} associated with the I + F transition, such that $|(\Omega - \omega_{FI}) / (\Omega + \omega_{FI})| \ll 1$ (resonance or rotating-wave approximation). (3) Any Doppler dephasing or atomic decay can be neglected on the time scale of the duration of a collision, τ_c . (4) The laser pulse duration τ_L is much greater than the collision duration, implying that a collision is totally completed during the laser pulse. (5) Only detunings in the line wings, $|\Delta| \tau_c > 1$, are considered. Conditions (4) and (5), taken together, imply that $|\Delta| \tau_L \gg 1$, which in turn, implies that there is negligible transition amplitude in the absence of collisions. (6) The A-A' internuclear separation R is calculated along a classical trajectory and can be considered as an explicit function of time. (7) In the absence of the radiation field, collisions do not result in transitions out of initial state $|I\rangle$ (there are no resonant A-A' collisions).

Both CARE and LICET can be treated by a similar formalism. The Hamiltonian for the A-A' system interacting with a radiation field is

$$H = H_0(\vec{r}) + H_c[\vec{r}, \vec{R}(t)] - \vec{\mu}_T \cdot \vec{E}(R, t) \quad (5)$$

where H_0 is the sum of atomic Hamiltonians for atoms A and A' (\vec{r} represents the electronic coordinates of either atom A or A'), $H_c[\vec{r}, \vec{R}(t)]$ is the A-A' collisional Hamiltonian, $\vec{\mu}_T = \vec{\mu} + \vec{\mu}'$ is the sum of dipole operators $\vec{\mu}$ and $\vec{\mu}'$ for atoms A and A', respectively, and $\vec{E}(t)$ is the applied field, assumed to be of the form

$$\vec{E}(t) = \frac{1}{2} [\vec{E}_0 e^{-i\Omega t} + \vec{E}_0^* e^{i\Omega t}]. \quad (6)$$

It is convenient to expand the wave function as

$$|\psi(t)\rangle = \sum_E a_E(t) |E(R)\rangle, \quad (7)$$

where $|E(R)\rangle$ is a short-hand notation for $|E[R(t)]\rangle$. The quantity $|E(R)\rangle$ is an instantaneous eigenket of $(H_0 + H)$; that is

$$[H_0 + H_c(R)] |E(R)\rangle = E(R) |E(R)\rangle. \quad (8)$$

When Eq. (7) is substituted into the Schrödinger equation and Eq. (8) is used, one finds that the $a_E(t)$ satisfy

$$\begin{aligned}
i\hbar \dot{a}_E(t) = & E(R)a_E(t) - \sum_{E'} \langle E(R) | \vec{\mu}_T | E'(R) \rangle \cdot \vec{E}(t) a_{E'}(t) \\
& - i\hbar \sum_{E' \neq E} \langle E(R) | \frac{\partial | E'(R) \rangle}{\partial t} a_{E'}(t) . \quad (9)
\end{aligned}$$

It is noted that $H_c(R) \sim 0$ as $R \sim \infty$; consequently, the eigenkets $|E(R)\rangle$ reduce to the composite state eigenkets $|E\rangle = |ee'\rangle$ of H_0 as R approaches infinity.

By assumption, collisions do not produce any transitions in the composite AA' system in the absence of any radiation. Consequently, the last term in Eq. (9) can be dropped since it corresponds precisely to transitions of this nature. The resulting equation for $a_E(t)$,

$$i\hbar \dot{a}_E(t) = E(R)a_E(t) - \sum_{E'} \langle E(R) | \vec{\mu}_T | E'(R) \rangle \cdot \vec{E}(t) a_{E'}(t), \quad (10)$$

can be given a simple interpretation in terms of a quasimolecular picture of the reaction. The A-A' system can be viewed as a quasimolecule with energy eigenvalues $E(R)$ and corresponding eigenkets $|E(R)\rangle$. The field induces transitions between quasimolecular states $|E(R)\rangle$ and $|E'(R)\rangle$ which depends on the dipole matrix element $\langle E(R) | \vec{\mu}_T | E'(R) \rangle$. The validity condition for Eq. (10) is discussed in more detail in Sec. III.

In the rotating-wave or resonance approximation, Eq. (10) yields the following set of time-evolution equations for the initial and final-state amplitudes:

$$i\hbar \dot{a}_I = E_I(R)a_I - \hbar \chi_T^*(R) e^{i\Omega t} a_F \quad (11a)$$

$$i\hbar \dot{a}_F = E_F(R)a_F - \hbar \chi_T(R) e^{-i\Omega t} a_I . \quad (11b)$$

The Rabi frequency $\chi_T[R(t)]$ appearing in Eq. (11) is defined by

$$\chi_T(R) = \frac{\langle F(R) | \vec{\mu}_T | I(R) \rangle \cdot \vec{E}_0}{2\hbar} , \quad (12)$$

where the field amplitude \vec{E}_0 is evaluated at the time of the collision. It will prove useful to define

$$\begin{aligned}
\omega_{FI}(R) = & [E_F(R) - E_I(R)]/\hbar \\
= & \omega_{FI} + U_{FI}(R) , \quad (13)
\end{aligned}$$

where $\omega_{FI}(R)$ is the transition frequency in the molecular basis, ω_{FI} is the transition frequency in the separated-atom basis [$\omega_{FI}(R) \sim \omega_{FI}$ as $R \sim \infty$], and $U_{FI}(R) = \omega_{FI}(R) - \omega_{FI}$ is the collision-induced modification of the separated-atom transition frequency. We are interested in the solution of Eq. (11) for $|a_F(\infty)|$ to lowest order in \vec{E}_0 , assuming the atoms are in state $|I\rangle = |ii'\rangle$ at $t = -\infty$ (before the collision). This solution is given by

$$|a_F(\infty)| = \left| \int_{-\infty}^{\infty} \chi_T[R(t)] e^{-i/\hbar \int_0^t \Delta[R(t')] dt'} dt \right|, \quad (14)$$

where

$$\begin{aligned} \Delta(R) &= \Omega - \omega_{FI}(R) \\ &= \Delta - U_{FI}(R), \end{aligned} \quad (15)$$

and Δ is given by Eq. (4).

It can be seen from Eqs. (14) and (15) that the final-state amplitude $a_F(\infty)$ can be viewed as a single-photon transition in the A-A' quasimolecule between levels separated in frequency by $\omega_{FI}(R)$. The coupling strength is given by $\chi_T(R)$. The detailed structure of the CARE or LICET cross section, defined as the value of $|a_F(\infty)|^2$ averaged over the distribution of collision impact parameters and A-A' relative speeds, depends on the functional form of $\chi_T(R)$ and $U_{FI}(R)$. In the line wings ($|\Delta| \tau_c > 1$), however, the qualitative dependence of both the LICET and CARE cross sections on Δ is similar. Suppose, for example, that the relative collisional shift $U_{FI}(R)$ increases monotonically with decreasing R (see Fig. 2).

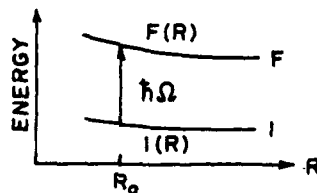


Fig. 2. Quasimolecular energy levels for a laser-assisted collision. The frequency shift $U_{FI}(R) = \omega_{FI}(R) - \omega_{FI}$ increases with decreasing R . For the frequency shown, the excitation occurs at an internuclear separation $R \approx R_0$.

Then, there are internuclear separations for which $\Delta(R) = 0$ if $\Delta > 0$, but none if $\Delta < 0$. Another way of stating this result is that the applied field can be resonant with the A-A' quasimolecule for $\Delta > 0$ but not for $\Delta < 0$, if $U_{FI}(R) > 0$. As a consequence of this asymmetry, the CARE and LICET cross sections exhibit a marked asymmetry for detunings $|\Delta|\tau_c > 1$. For the illustrative example given above, the quasistatic wing ($\Delta\tau_c > 1$) falls off slowly with increasing $|\Delta|\tau_c$ owing to the $\Delta(R) = 0$ resonances, while the antistatic wing ($\Delta\tau_c < -1$) falls off rapidly with increasing $|\Delta|\tau_c$ owing to the lack of such resonances. A typical LAC profile is shown in Fig. 1, exhibiting a power law fall-off with $\Delta\tau_c$ for $\Delta\tau_c > 1$ and an exponential fall-off with $\Delta\tau_c$ for $\Delta\tau_c < -1$. [If $U_{FI}(R)$ decreases monotonically with decreasing R, the quasistatic wing occurs for $\Delta\tau_c < -1$ and the antistatic wing for $\Delta\tau_c > 1$.]

From this point onward, I should like to focus the discussion on the quasistatic wing of the LAC profiles. In the quasistatic wing, it is possible to obtain an approximate expression for the LAC cross section using the method of stationary phase. If $\Delta\tau_c \gg 1$, the major contribution to the integral (14) comes from those values of $t = t_0$ (or internuclear separations $R = R_0$) for which $\Delta(R_0) = 0$ or, equivalently, for which $\Omega = \omega_{FI}(R_0)$. For the energy levels shown in Fig. 2, there are two times, symmetric about $t = 0$, for which $\Omega = \omega_{FI}(R)$, provided that $\Delta > 0$ and $\omega < \omega_{FI}(b_0)$, where b_0 is the A-A' internuclear separation at $t = 0$. Neglecting any interference effects between the contributions from the two crossing points, it is possible to integrate Eq. (3) by the method of stationary phase (assuming $\Delta\tau_c \gg 1$) take its square modulus, and average over impact parameter. In that manner, using Eq. (15) and assuming straight-line collision trajectories, one obtains the (speed-dependent) LAC cross section

$$\sigma = \frac{8|\chi_T(R_0)|^2 \pi^2 R_0^2}{v|dU_{FI}(R_0)/dR_0|} \quad (16)$$

where v is the A-A' relative speed, and R_0 is defined by $\Omega = \omega_{FI}(R_0)$ or, equivalently, by $\Delta = U_{FI}(R_0)$.

Equation (16) could have been predicted using dimensional analysis. The cross section depends on the square of the radius of excitation R_0^2 and the square of the product of coupling strength $\chi_T(R_0)$ times the time spent in the crossing region. The time spent in the crossing region varies as

$|dU_{FI}(R_0)/dt_0|^{-1/2} = [v|dU_{FI}(R_0)/dR_0|]^{-1/2}$. It remains to specify $\chi_T(R)$ and $\omega_{FI}(R)$.

III. Evaluation of the Cross Section

In order to calculate $\chi_T(R)$ and $U_{FI}(R)$, one must find the quasimolecular eigenkets and eigenenergies $|E(R)\rangle$ and $E(R)$, respectively. To facilitate this calculation, it is useful to recall Eq.(9), which gives the "exact" time development in the quasimolecular basis. The transition from Eq. (9) to (10) was based on the assumption that the quasimolecular states are not coupled in the absence of any radiation fields - in other words, they are adiabatic states. For the problem under discussion, the adiabaticity requirement reduces to

$$\begin{aligned} |\omega_{IE}(R)\tau_c| &\gg 1, E \neq I ; \\ |\omega_{FE}(R)\tau_c| &\gg 1, E \neq F ; \end{aligned} \quad (17)$$

where $E(R)$ is the eigenenergy of an arbitrary level in the quasimolecular basis. It is assumed that the adiabaticity conditions (17) are always satisfied.

The adiabatic eigenkets and eigenenergies are solutions of Eq.(8); they are simply the eigenkets and eigenenergies of the Hamiltonian $[H_0 + H_c(\vec{r}, R)]$. Within the context of the model, the quantities $E(R)$ and $|E(R)\rangle$ can be calculated using perturbation theory in the *separated*-atom basis. The manner in which perturbation theory is applied depends critically on the coupling matrix elements $V_{IE}(R) = (H_c)_{IE}/\hbar$ or $V_{FE}(R) = (H_c)_{FE}/\hbar$. In conventional "two-state" theories of LAC, it is implicitly assumed that $|V_{\alpha E}(R)| \ll |\omega_{\alpha E}|$ ($\alpha = I, F$). In the modified "three-state" theory of LAC to be discussed below, it is assumed that there is one state D for which the inequality $|V_{\alpha D}(R)| \ll |\omega_{\alpha D}|$ ($\alpha = I$ or F) fails to hold. I consider each case separately.

A. Conventional Two-State Theory

The condition $|V_{\alpha E}(R)| \ll |\omega_{\alpha E}|$ ($\alpha = I, F$) is sufficient for carrying out non-degenerate perturbation theory on the Hamiltonian $H_0 + H_c$. Defining

$$V_{EE'}(R) = [H_c(R)]_{EE'}/\hbar, \quad (18)$$

one can easily obtain

$$|E(R)\rangle = |E\rangle + \sum_{E' \neq E} \frac{V_{E'E}(R)}{\omega_{EE'}} |E'\rangle, \quad (19)$$

and

$$E(R) = E + U_E(R), \quad (20a)$$

with

$$U_E(R) = \sum_{E' \neq E} \frac{|V_{EE'}(R)|^2}{\omega_{EE'}}. \quad (20b)$$

The collision-induced frequency shift $U_{FI}(R)$ is given by

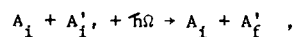
$$U_{FI}(R) = U_F(R) - U_I(R) \quad (21)$$

which, combined with (20b), yields

$$U_{FI}(R) = \sum_E \left[\frac{|V_{FE}(R)|^2}{\omega_{FE}} - \frac{|V_{IE}(R)|^2}{\omega_{IE}} \right] \quad (22)$$

For a dipole-dipole collisional interaction, $V_{FE}(R)$ [or $V_{IE}(R)$] varies as R^{-3} and $U_{FI}(R)$ varies as R^{-6} , typical of a van der Waals interaction.

The value of $\chi_T(R)$ depends on the specific excitation scheme. The atomic energy-level diagram appropriate to the CARE reaction,



is shown in Fig. 3(a). The initial state is $|I\rangle = |ii'\rangle$, the final state

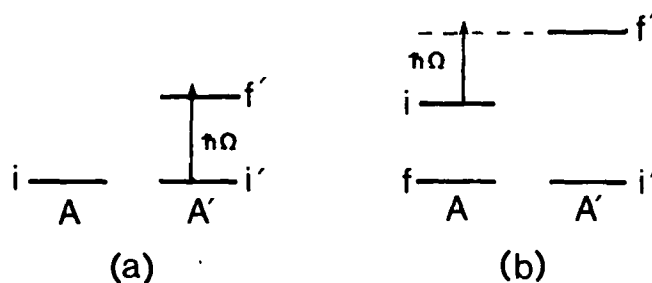


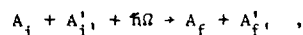
Fig. 3. Energy level diagrams for laser-assisted collisions:
 (a) CARE reaction $A_i + A_i' + \hbar\Omega \rightarrow A_f + A_f'$,
 (b) LICET reaction $A_i + A_i' + \hbar\Omega \rightarrow A_f + A_f'$.

is $|F\rangle = |if'\rangle$, and atomic states $|i'\rangle$ and $|f'\rangle$ have opposite parity. In this limit, it follows from Eqs. (12) and (19) that, to lowest order in the collisional interaction, the Rabi frequency is independent of R . Explicitly, one finds

$$\begin{aligned}\chi_T &= \langle F | \vec{u}_T | I \rangle \cdot \vec{E}_0 / 2\hbar \\ &= \langle f' | \vec{u}' | i' \rangle \cdot \vec{E}_0 / 2\hbar.\end{aligned}\quad (23)$$

For a collisional shift operator $U_{FI}(R)$ which varies as R^{-n} ($n \geq 3$), the CARE cross section, as given by Eq. (16), falls off as $|\Delta|^{-(1 + \frac{3}{n})}$ in the quasi-static wing.

The situation changes if one considers the LICET reaction:



whose energy level diagram is shown in Fig. 3(b). Since both atoms change their internal states, it follows immediately that

$$\langle F | \vec{u}_T | I \rangle = \langle ff' | \vec{u} + \vec{u}' | ii' \rangle = 0.\quad (24)$$

Thus, in contrast to CARE, the Rabi frequency $\chi_T(R)$ given by Eqs. (12) and (19) vanishes asymptotically as $R \sim \infty$. The combined radiative-collisional coupling $\chi_T(R)$, obtained from Eqs. (12) and (19), is

$$\chi_T(R) = \sum_E \left[\frac{\chi_{FE}^V E I}{\omega_{IE}} + \frac{\chi_{FE}'^V E I}{\omega_{IE}} + \frac{V_{FE}^X E I}{\omega_{FE}} + \frac{V_{FE}'^X E I}{\omega_{FE}} \right]\quad (25)$$

where

$$\chi_{EE'} = \langle E | \vec{u} | E' \rangle \cdot \vec{E}_0 / 2\hbar;\quad (26a)$$

$$\chi_{EE}' = \langle E | \vec{u}' | E' \rangle \cdot \vec{E}_0 / 2\hbar\quad (26b)$$

For a Rabi frequency $\chi_T(R)$ which varies as R^{-m} and a collisional shift frequency $U_{FI}(R)$ which varies as R^{-n} ($m, n \geq 3$), the LICET cross section,

as given by Eq. (16), falls off as $|\Delta|^{-(1 + \frac{3}{n} - \frac{2m}{n})}$ in the quasistatic wing.

The results of this sub-section have been categorized as those of a "two-

state" theory. The label "two-state" refers to the separated-atom basis. As long as $|V_{\alpha E}(R)| \ll |\omega_{\alpha E}|$ ($\alpha = I, F$), all separated-atom states other than $|I\rangle$ and $|F\rangle$ are negligibly populated *during* and following the collision. In other words, the problem can be reduced to an effective two-state problem in the separated-atom basis. It should be noted that, in the quasimolecular basis, the problem is *always* an effective two-level problem involving states $|I(R)\rangle$ and $|F(R)\rangle$ provided the adiabaticity conditions (17) are valid.

B. Modified Three-State Theory

I now consider the energy level diagrams shown in Figs. 4 and 5, respectively. In both Fig. 4 (CARE reaction) and Fig. 5 (LICET reaction), there is a single intermediate state $|D\rangle$ that is nearly-resonant with either the initial or final state. For example, in Fig. 4, state $|D\rangle = |di'\rangle$ is nearly resonant with state $|F\rangle = |if'\rangle$ while, in Fig. 5(b), state $|D\rangle = |fd'\rangle$ is nearly resonant with state $|I\rangle = |ii'\rangle$.

The term "nearly-resonant" must be made more precise. Since we are assuming adiabaticity [inequalities (17)], the detunings ω_{DI} and ω_{DF} must be large enough to satisfy

$$|\omega_{DI}| \gg 1; |\omega_{DF}| \gg 1. \quad (27)$$

On the other hand, it is assumed that ω_{DI} or ω_{DF} is sufficiently small to insure that $|V_{\alpha D}(R)| \ll |\omega_{\alpha D}|$ ($\alpha = I$ or F). In the quasistatic wing, the internuclear separation at which the transition takes place is determined by the condition $\Delta = U_{FI}(R_0)$. If we set $V_D(R) = U_{FI}(R_0)$, then, in the quasistatic wing, the "nearly-resonant" condition becomes

$$|\omega_{\alpha D}| \ll |\Delta|; \alpha = I \text{ or } F. \quad (28)$$

In other words, for a range of detunings

$$|\Delta| = |\omega_{\alpha D}| \gg \tau_c^{-1}; \alpha = I \text{ or } F, \quad (29)$$

the collision is both adiabatic and "nearly-resonant".

The collision is adiabatic in the sense that the quasimolecular levels are not coupled in the absence of the radiation field. Since the quasimolecular states go over into the separated-atom states as $R \rightarrow \infty$, the

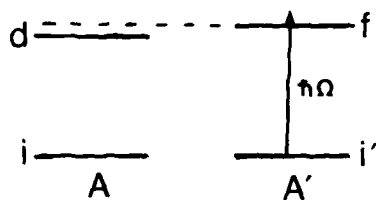


Fig. 4. Excitation scheme for the Care reaction $A_i + A'_i + \hbar\Omega \rightarrow A_f + A'_f$, in which state $|D\rangle = |di'\rangle$ is nearly resonant with final state $|F\rangle = |if'\rangle$.

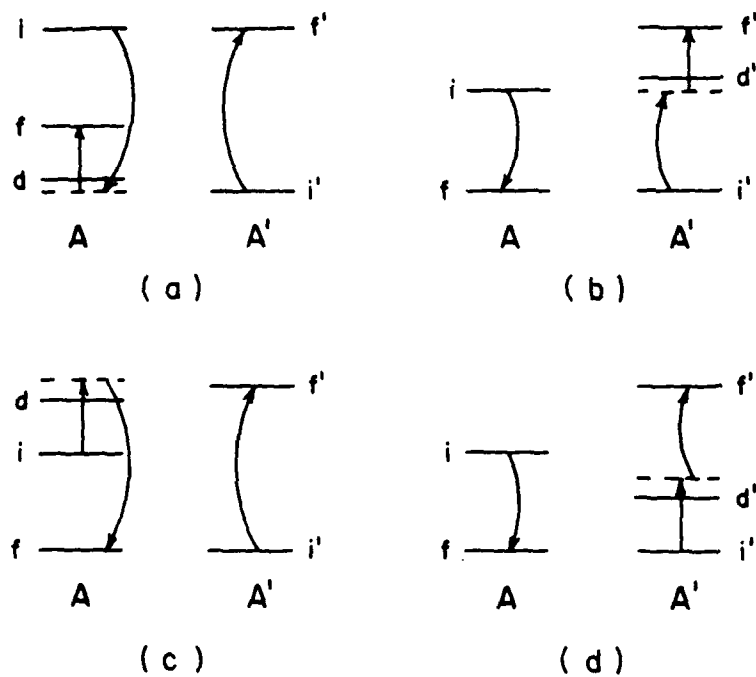


Fig. 5. Various LICET excitation schemes for the reaction $A_i + A'_i + \hbar\Omega \rightarrow A_f + A'_f$. The curved arrows represent the collisional coupling and the straight arrows the radiative coupling. The reactions proceed via an intermediate state which is nearly resonant with either the initial or final state.

adiabaticity condition also implies that, in the absence of the radiation field, the separated-atom states are unchanged following a collision. However, inequality (28) insures that $|v_{\alpha D}(R)| > |\omega_{\alpha D}|$ (from this point onward, it is assumed that $\alpha = I$ or F) during the collision. This implies that the coupling matrix element connecting states $|\alpha\rangle$ and $|D\rangle$ is comparable to the frequency separation of those states. Consequently, it is no longer permissible to use non-degenerate perturbation theory to calculate $|\alpha(R)\rangle$ and $\alpha(R)$. Moreover, separated-atom state $|D\rangle$ acquires a non-negligible population during the collision (a population which vanishes asymptotically as $R \sim \infty$). The fact that it is no longer a good approximation to neglect state $|D\rangle$ population during the collision is the reason why the modified theory is referred to as a "three-state" theory.

It is now assumed that, owing to the fact that state $|D\rangle$ is nearly resonant with state $|I\rangle$ or $|F\rangle$, all intermediate states other than state $|D\rangle$ contribute negligibly to the CARE and LICET reactions. For the experiments to be discussed in Sec. IV, this approximation is sufficiently accurate to illustrate the relevant physical features of the LAC cross sections. The quasimolecular energy level diagrams corresponding to these reactions are shown in Fig. 6. Figure 6(a) corresponds to the LICET

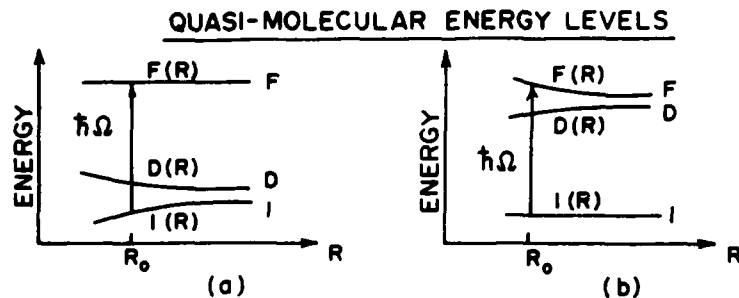


Fig. 6. Quasimolecular energy levels as a function of A-A' internuclear separation R . The asymptotic values I , D , and F are the energies of the composite atomic states. Fig. 6(a) corresponds to the LICET excitation schemes of Figs. 5(a) and 5(b), while Fig. 6(b) corresponds to the LICET excitation schemes of Figs. 5(c) and 5(d) and to the CARE excitation scheme of Fig. 4. For the frequency shown, the $I(R) \rightarrow F(R)$ transition is resonant at $R = R_0$.

excitation schemes of Figs. 5(a) and 5(b) while Fig. 6(b) corresponds to the LICET excitation schemes of Figs. 5(c) and 5(d) and to the CARE excitation scheme of Fig. 4. The level repulsion of the nearly-degenerate levels is seen in these diagrams.

The collision-induced level shift $U_{FI}(R) = [\omega_{FI}(R) - \omega_{FI}]$ and coupling strength $\chi_T(R)$ must now be calculated using non-degenerate perturbation theory in the α -D subspace, where

$$\alpha = I; \text{ Figs. 5(a), (b)} \quad (30a)$$

$$\alpha = F; \text{ Figs. 4, 5(c), 5(d)} \quad (30b)$$

To simplify the notation, I will carry out the calculation for the level scheme of Fig. 6(a); the level scheme of Fig. 6(b) can be treated in a completely analogous fashion. Since the only non-negligible coupling is between states $|I\rangle$ and $|D\rangle$, it follows immediately that

$$|F(R)\rangle \approx |F\rangle; U_F(R) = 0. \quad (31)$$

If the energy of state $|I\rangle$ is set equal to zero, the Hamiltonian (in frequency units) in the I-D subspace that must be diagonalized is

$$H = \begin{pmatrix} 0 & V \\ V & \omega_{DI} \end{pmatrix}, \quad (32)$$

where $V(R) = V_{ID}(R) = V_{DI}(R)$. The eigenfrequencies and eigenkets of the Hamiltonian (32) are given by:

$$\omega_I(R) = [\omega_{DI} - \omega_{DI}(R)]/2 \quad (33a)$$

$$\omega_D(R) = [\omega_{DI} + \omega_{DI}(R)]/2 \quad (33b)$$

and

$$|I(R)\rangle = \cos[\theta(R)]|I\rangle + \sin[\theta(R)]|D\rangle \quad (34a)$$

$$|D(R)\rangle = -\sin[\theta(R)]|I\rangle + \cos[\theta(R)]|D\rangle \quad (34b)$$

where

$$\sin[\theta(R)] = \frac{1}{\sqrt{2}} \left[1 - \frac{\omega_{DI}}{\omega_{DI}(R)} \right]^{1/2} \quad (35)$$

and

$$\omega_{DI}(R) = \{\omega_{DI}^2 + 4[V(R)]^2\}^{1/2} \quad (36)$$

The transition occurs at internuclear separations given by $\Omega = \omega_{FI}(R_0)$ or, equivalently, by

$$\Delta = U_{FI}(R_0) = -\omega_I(R_0) \quad (37)$$

Since R_0 is defined by Eq. (37) and since $dU_{FI}(R_0)/dR_0 = -d\omega_I(R_0)/dR_0$ can be evaluated by using Eqs. (33a), (36), and (37), the only remaining quantity to specify is $\chi_T(R_0)$.

In CARE, states $|I\rangle$ and $|F\rangle$ are directly coupled by the field. In LICET, states $|I\rangle$ and $|F\rangle$ are not directly coupled by the fields; rather it is states $|D\rangle$ and $|F\rangle$ which are coupled by the field (see Fig. 5). It follows from Eqs. (12), (31) and (34) that

$$\chi_T(R) = \chi_T(FI)\cos[\theta(R)] ; \quad \text{CARE} \quad (38a)$$

$$\chi_T(R) = \chi_T(FD)\sin[\theta(R)] ; \quad \text{LICET} \quad (38b)$$

where

$$\chi_T(E E') = \langle E | \vec{\mu}_T | E' \rangle \cdot \vec{E}_0 / 2\hbar . \quad (39)$$

Combining Eqs. (16) and (33) - (39), one obtains the LAC cross sections

$$\sigma = \frac{4 |\chi_T(FI)|^2 \pi^2 R_0^2 (\omega_{DI} + \Delta)}{|vV(R_0)dv(R_0)/dR_0|} ; \quad \text{CARE} ; \quad (40a)$$

$$\sigma = \frac{4 |\chi_T(FD)|^2 \pi^2 R_0^2 \Delta}{|vV(R_0)dv(R_0)/dR_0|} ; \quad \text{LICET} , \quad (40b)$$

where

$$|V(R_0)| = [\Delta(\omega_{DI} + \Delta)]^{1/2} . \quad (41)$$

For a dipole-dipole collisional interaction,

$$V(R) = -C/R^3, \quad C > 0 ; \quad (42)$$

Eqs. (40) reduce to

$$\sigma = \frac{4}{3} \frac{\pi^2 |\chi_T(FI)|^2 |C|}{v \Delta^{3/2} (\Delta + \omega_{DI})^{1/2}} ; \quad \text{CARE}, \quad (43a)$$

$$\sigma = \frac{4}{3} \frac{\pi^2 |\chi_T(FD)|^2 |C|}{v \Delta^{3/2} (\Delta + \omega_{DI})^{3/2}} ; \quad \text{LICET} . \quad (43b)$$

To arrive at the corresponding result for the level scheme of Fig. 6(b), one simply replaces ω_{DI} by ω_{FD} and $\chi_T(FD)$ by $\chi_T(DI)$ in these equations. If $\omega_{DI} \gg \Delta$, as is commonly assumed in conventional "two-state" theories

of CARE and LICET, then $\sigma \sim \Delta^{-3/2}$ for CARE and $\sigma \sim \Delta^{-1/2}$ for LICET. However, if $\Delta = \omega_{DI}$, the quasistatic wing falls off more steeply than $\Delta^{-3/2}$ (CARE) or $\Delta^{-1/2}$ (LICET) and the conventional two-state CARE or LICET theories are no longer valid. Since $\Delta \approx \omega_{DI}$ in all high resolution LICET experiments reported to date, it is not surprising that the conventional theory fails to satisfactorily explain the data. On the other hand, Eq. (43b), which represents a simple extension of the theory to account for the fact that Δ and ω_{DI} may be of comparable magnitude, provides very good quantitative agreement with experiment.

IV. Comparison with Experiment

I now wish to compare Eqs. (43) with some of the available experimental data. Most CARE experiments are carried out in the absence of a nearly-resonant intermediate state. There is, however, at least one CARE experiment that should be approximately described by Eq. (43a). Niemax [15] studied CARE on the $\lambda = 459.5\text{nm}$ line of Eu perturbed by Sr. This reaction corresponds to Fig. 4 with $\omega_{FD} = 63\text{ cm}^{-1}$; a detuning range $10\text{ cm}^{-1} < \Delta < 200\text{ cm}^{-1}$ was reported. The quasistatic wing exhibited a $\Delta^{-1.5}$ fall-off for $\Delta < 50\text{ cm}^{-1}$ and a Δ^{-2} fall-off for $\Delta > 50\text{ cm}^{-1}$, in relatively good agreement with Eq. (43a) (with ω_{DI} replaced by ω_{FD}), which predicts a similar behaviour, with a crossover from $\Delta^{-1.5}$ to Δ^{-2} behaviour at $\Delta = 63\text{ cm}^{-1}$.

A comparison between theory and experiment is presented in Fig. 7 for Eu-Sr [10], Na-Ca [11], and Sr-Li [12] LICET reactions. The Eu-Sr reaction corresponds to the level scheme of Fig. 5(b) with the frequency mismatch ω_{DI} equal to -63 cm^{-1} ; a detuning range $-55\text{ cm}^{-1} < \Delta < -10\text{ cm}^{-1}$ was reported [10]. The comparison between theory [Eq.(43b)] and experiment [$(-\Delta)^{-0.85}$ dependence] is shown in Fig. 7(a). This experiment was recently repeated by Matera et al. [16], again showing good agreement with Eq. (43b). (b) The Na-Ca reaction corresponds to the level scheme of Fig.5(d) with $\omega_{FD} = 94\text{ cm}^{-1}$; a detuning range $\Delta < 60\text{ cm}^{-1}$ was reported [11]. As shown in Fig. 7(b), agreement between theory [Eq. (43b) with ω_{DI} replaced by ω_{FD}] and experiment [$\Delta^{-0.8}$ dependence] is very good. (c) The Sr.-Li reaction corresponds to the level scheme of 5(d) with $\omega_{FD} = 21\text{ cm}^{-1}$; a detuning range $\Delta < 50\text{ cm}^{-1}$ was reported [12]. A comparison between theory and experiment is given in Fig. 7(c), where the varying slope of $\log(\sigma)$ vs $\log(\Delta)$ predicted by Eq. (43b) is clearly seen in the data. [Equation

(43b) is not strictly valid for $\Delta < 5 \text{ cm}^{-1}$, since the quasistatic assumption ($\Delta\tau_c \gg 1$) used in its derivation fails in this detuning range for the Sr-Li reaction.]

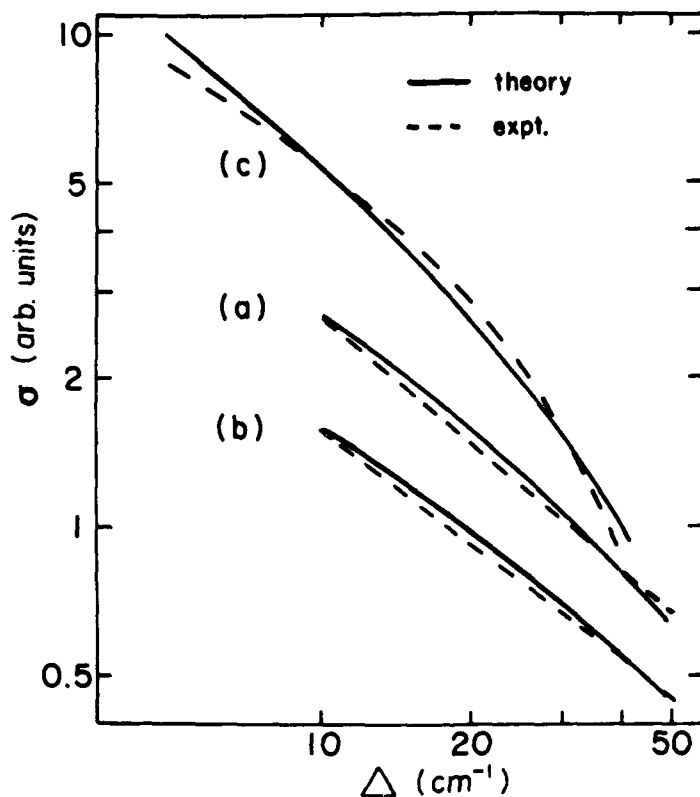


Fig. 7. LICET cross section σ (arbitrary units) as a function of detuning $\Delta(\text{cm}^{-1})$ for energy defects (a) $\omega_{DI} = 63 \text{ cm}^{-1}$ (Eu-Sr), (b) $\omega_{FD} = 94 \text{ cm}^{-1}$ (Na-Ca) and (c) $\omega_{FD} = 21 \text{ cm}^{-1}$ (Sr-Li). The point at $\Delta = 10 \text{ cm}^{-1}$ is chosen to normalize the theoretical and experimental curves.

V. Discussion

It has been shown that the conventional "two-state" theory of laser-assisted collisions (LAC) is no longer valid for detunings $|\Delta|$ which are

comparable with the frequency separation between the initial state $|I\rangle$ (or final state $|F\rangle$) and some intermediate state $|D\rangle$ in the CARE and/or LICET reactions. In such cases a "three-state" theory of LAC is needed, in which one allows for state $|D\rangle$ to have a non-negligible population during the collision. Since most LICET experiments have been carried out for a detuning range in which the "three-state" theory is needed, it is not surprising that the conventional two-state theory failed to correctly describe the detuning dependence in the quasistatic wing. The modified theory presented in this review gives very good overall agreement with experiment. Although many approximations were made in arriving at the LAC cross sections, computer solutions [14] of the appropriate equations indicate that the approximations are satisfactory for the experimental parameters of interest.

The three-state theory can be extended in a number of ways. (1) It is possible to formulate a strong-field version of the theory. This is particularly important since the strong-field data of Dorsch *et.al.* [12] does not agree with predictions of the conventional theory. The experimental profiles do not become symmetric and do not narrow with increasing field strength, as predicted by the conventional theory. Preliminary calculations [17] using the three-state theory do not appear to resolve this discrepancy. (2) The theory can be extended to include effects arising from the magnetic degeneracy of the levels. The coupling parameter $V(R) = [H_c(R)]_{ID}$ is replaced by a matrix which couples the various magnetic sublevels of states $|I\rangle$ and $|D\rangle$. (3) Finally, one can remove the adiabaticity requirement and allow population to be transferred to the nearly-resonant intermediate state $|D\rangle$ following a collision. In this limit, the quasimolecular states are not necessarily the most convenient basis states since they are coupled for at least some range of inter-nuclear separations.

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