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Nonadiabatic theory of atomic line broadening: Final-state distributions and the polarization of redistributed radiation

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The close-coupled theory of atomic collisions in the presence of a radiation field may be used to calculate the distribution of final atomic states which results from absorption of polarized light during a collision. The theory applies equally well to optical collisions (line broadening) and to radiative collisions (laser-induced collisional energy transfer). For an optical collision the detuning $\omega-\omega_\infty$ is restricted to be larger than either the Rabi frequency or the widths due to natural, Doppler, or pressure broadening. The radiation field is assumed to be weak enough that the transition probabilities are linear in field intensity. The molecular picture is emphasized in which the wave function is expanded in a basis of field-free molecular states and the Hamiltonian is blocked in accordance with molecular quantum numbers. The quantities needed to predict experimental observables are reduced radiative scattering S-matrix elements s_ω in the asymptotic Hund's case-(e) representation. The theory of product orientation and alignment is equivalent to that which has been developed for molecular photodissociation. It requires coherent sums of s_ω matrix elements from different transition branches, that is, for P-, Q-, and R-type transitions corresponding to changes of -1, 0, and $+1$ in total molecular angular momentum. On the other hand, the total absorption coefficient and the branching ratio to different final fine-structure states irrespective of orientation or alignment depend on incoherent sums of the same matrix elements.

I. INTRODUCTION

The absorption of light during an atomic collision has long been the subject of line-broadening experiments and theory. Such a collision may be described by the equation

$$A_0+B_0+n_\lambda\hbar\omega\rightarrow A+B+(n_\lambda-1)\hbar\omega\ , \tag{1}$$

where n_λ represents the number of photons in mode λ of the radiation field with frequency ω and polarization $\hat{e}_q$. For an ordinary line-broadening collision, also called an optical collision,[1,2] the perturber atom does not change state, $B=B_0$, and the photon frequency is tuned near (but we assume not equal to) the frequency ω_∞ for an allowed transition of atom A,

$$\hbar\omega_\infty=E^A-E_0^A\ . \tag{2}$$

For a radiative collision,[1,3] both atoms A and B change state, and ω is tuned near the atomic difference frequency,

$$\hbar\omega_\infty=E^A+E^B-E_0^A-E_0^B\ . \tag{3}$$

Several recent experiments have studied the atomic fluorescence (redistribution) following absorption in the profile wings. Polarized fluorescence has been measured from excited Sr or Ba ${}^1P_1^0$ atoms following wing absorption of polarized laser light tuned near the ${}^1P$-${}^1S$ resonance line broadened by collisions with rare-gas atoms.[4-7] The Na+Ar system has also been studied by near-wing polarization redistribution experiments[8] and by measurement of the ${}^2P_{1/2}/{}^2P_{3/2}$ branching ratio following far-wing absorption.[9] These experiments represent optical collisions. Similar polarization redistribution experiments have also been suggested as a useful way to study radiative collisions,[10] and such an experiment has been reported.[11] These experiments, which probe the final-state distribution following absorption by the transient AB quasimolecule formed during the collision, may be expected to yield more information about collision dynamics and molecular interactions than measurement of the line profile alone.[6]

We have recently used the close-coupled theory of collisions in a radiation field[12-15] to develop a nonadiabatic theory of collision-broadened atomic line profiles (henceforth called I).[16] The theory gives a complete description of the nonadiabatic molecular dynamics for a single binary collision in the presence of a radiation field. The results of the theory are the state-to-state cross sections for the radiatively assisted collision (1). These can be used to predict the distribution of final atomic states and polarization of emitted radiation for both optical and radiative collisions. This theory has been used to obtain numerical results for Sr+Ar which have been briefly reported elsewhere.[17] Recent application of the theory of collisions in a radiation field has also been made to calculate the ${}^2P_{1/2}/{}^2P_{3/2}$ branching ratio for Na+Ar[18] and for Na plus He, Ne, and Ar.[19]

A complete density-matrix theory of radiative redistribution, including the effect of atomic degeneracy, has recently has given by Burnett and Cooper.[20,21] If the binary collision approximation is made, then the parameters required by their theory can be calculated by considering only the properties of the quasimolecule AB. Our stationary-state scattering formulation may thus be expected to predict the same observables as their theory when applied with the appropriate restrictions. We will confine ourselves in this paper to giving a cross-section formulation of the coherent final-state distributions which result from absorption of polarized light during an atomic collision. Thus we predict the total fluorescence intensity of polarized redistributed light at low pressure, but we are not concerned here with its spectral profile.

We will assume as in I that the incident radiation field is weak, and for an optical collision, detuned from the atomic resonance frequency by an amount much larger than the Rabi frequency Ω. Those assumptions ensure (a) that radiative couplings provide only a weak perturbation on collision dynamics and (b) the interaction of the radiation with the separated atoms can be neglected for the purpose of calculating the necessary cross sections.

As in I we emphasize the molecular picture with the close-coupled expansion of the wave function in terms of the field-free states of the AB molecule. The Hamiltonian matrix for the close-coupled scattering equation is blocked by the exact (conserved) field-free molecular quantum numbers, J, M, and p for the respective eigenstates of *molecular* total angular momentum, space fixed projection, and center of mass inversion of *all* coordinates. The field breaks the molecular symmetry according to the selection rules $\Delta J = b = 0, \pm 1$ and $\Delta M = q$. Thus, the radiation field induces transitions between initial and final manifolds of molecular states associated with such JMp blocks. The index b specifies the transition branch. We define a set of reduced radiative S-matrix elements s_ω^b in the asymptotic atomic channel state representation, which corresponds to a molecular Hund's case-(e) angular momentum coupling scheme. These yield the smallest number of dynamically independent radiative transition amplitudes required to calculate the state-to-state cross sections.

The theory of product distributions for a weak-field radiatively assisted collision of A and B is essentially equivalent to the theory of product distributions following photodissociation of the AB quasimolecule. Although the treatment of final-state interactions is the same for these two phenomena, they differ, of course, in the averaging over the ensemble of initial states. The "half-collision" picture, which is commonly applied to photodissociation,[22] can also be extended to the collision (1),[6] which may be viewed as a sequence of two half-collisions. This viewpoint will be developed explicitly in a subsequent paper on the basis of dynamical approximations. The present paper concerns itself with the expresssions which can be obtained solely by using the symmetries of the molecule and the dipole radiation field.

If we wish to calculate the orientation or alignment of a product atom, angular momentum algebra naturally leads to the same angular momentum transfer formulation which has been developed for photofragmentation studies.[23-25] Our goal is to calculate the collision cross sections for (1) which describe the production of final-state A atoms with electronic angular momentum j and space projection m. The m dependence is solely contained in geometric factors. All the required dynamical information is contained in reduced transfer cross sections $\sigma_\omega^t(j)$, which correspond to those occurring in photofragmentation theory. These transfer cross sections depend on coherent sums of reduced amplitudes s_ω^b from final-state Hamiltonian blocks for *different* branches b.

If we wish to calculate only the total cross sections for producing particular final fine-structure states irrespective of space projection m, it is convenient to define branch cross section $\sigma_\omega^b(j)$ for each transition branch. These are simpler than the transfer cross section $\sigma_\omega^t(j)$ in that they depend only on incoherent sums of squared amplitudes for a *single* branch. Furthermore, they are calculated in accordance with the blocking of the molecular Hamiltonian used to calculate the dynamics.

We will first consider the conditions under which the theory applies and obtain the expressions for the necessary cross sections. We include a discussion of Hund's case (e) and the case-(e) reduced radiative coupling matrix elements and selection rules. The relation to photofragmentation theory will be described, as well as some of the pertinent results of that theory. We conclude by a short discussion of the treatment of hyperfine effects and collisional depolarization.

II. THEORY

A. Conditions and assumptions

Let us assume that the collision partner B in (1) is a $j=0$ atom in both the initial and final states. This simplifying assumption eliminates one level of angular momentum recoupling in the theory and corresponds to the experimental situation in the alkali[8,9] or group-II metal[4-7] plus rare gas experiments, and also corresponds to the hypothetical radiative collision studied by Julienne[17] or the experimental one studied by Falcone *et al.*[3] Let the atom A be characterized by the initial-state angular momentum quantum numbers $j_0 m_0$ and the final-state quantum numbers jm. The choice of the space-fixed quantization axis for m_0 and m depends on the polarization $\hat{e}_q$ of the exciting light. For linearly polarized light the quantization axis $\hat{z}$ is chosen to be along $\hat{e}_q$,

$$\hat{e}_q = \hat{e}_0 = \hat{z} \ . \tag{4}$$

For circularly polarized light the $\hat{z}$ axis is chosen along the propagation direction of the light and

$$\hat{e}_q = \hat{e}_{\pm 1} = \frac{1}{\sqrt{2}}(\mp \hat{x} - i\hat{y}) \ . \tag{5}$$

We assume that the light is incident on a homogeneous cell containing a spatially isotropic distribution of atoms in their initial states, A_0 and B_0. Absorption by the AB quasimolecule formed during a collision of A_0 and B_0 ultimately produces a photofragment in an excited state of the A atom. We wish to calculate the following quantities, all of which can be measured by suitable experiments: (a) the total photon absorption coefficient, that is, the spectral profile; (b) the branching ratio to different final-state fine-structure components j summed over the distribution of m states, such as measured by the experiment of Havey *et al.*;[9] and (c) the orientation and/or alignment produced by the excitation, such as measured by Alford, *et al.*[5] The latter gives a measure of the distribution of final m states. We assume that the polarization of the final-state fluorescence is measured by detecting all spontaneously emitted photons over the whole profile in a transition to some final state A_f. All of the three observables above can be calculated in terms of averages over the state-to-state cross sections $\sigma(j,m \leftarrow j_0,m_0,\epsilon_0,\omega,q)$ for (1), where ϵ_0 is the incident kinetic energy.

For a weak radiation field the complete scattering wave function, expressed in the molecule-field product basis used in I,[12,16] is

$$\Psi^+(E)=e^{i\vec{k}_0\cdot\vec{R}}\,|j_0,m_0\rangle\,|n,\omega,q\rangle+\sum_{j_0',m_0'}\left[\frac{k_0}{k_0'}\right]^{1/2}\frac{e^{ik_0'R}}{R}f_c^+(j_0',m_0'\leftarrow j_0,m_0;\epsilon_0,\hat{k}_0,\hat{r})\,|j_0',m_0'\rangle\,|n,\omega,q\rangle$$
$$+\sum_{j,m}\left[\frac{k_0}{k_j}\right]^{1/2}\frac{e^{ik_jR}}{R}f_\omega^+(j,m\leftarrow j_0,m_0;\epsilon_0,q,\hat{k}_0,\hat{r})\,|j,m\rangle\,|n-1,\omega,q\rangle\ . \tag{6}$$

The first term represents an incident plane wave with atoms A and B in their initial states and the radiation field with n photons of frequency ω and polarization q. The second term with f_c^+ represents the elastically ($k_0'=k_0$) and inelastically ($k_0'\neq k_0$) scattered waves among the manifold of initial states. This scattering also occurs in the absence of the radiation field, and for weak fields is independent of the field parameters. For nondegenerate initial states, $j_0=0$, this term is elastic only. The third term with f_ω^+ is the one in which we are primarily interested. It contains the scattered wave for the final states produced by the absorption of one photon. The final-state kinetic energy is $\epsilon_j=\hbar^2k_j^2/2\mu$. The total energy of the system is

$$E=E_0^A+E_0^B+\epsilon_0+n\hbar\omega=E^A+E^B+\epsilon_j+(n-1)\hbar\omega\ . \tag{7}$$

Thus the detuning from the asymptotic transition frequency ω_∞ is

$$\hbar(\omega-\omega_\infty)=\epsilon_j-\epsilon_0\ . \tag{8}$$

The unit vectors $\hat{k}_0$ and $\hat{r}$ represent the respective directions of the incoming plane wave and outgoing scattered wave. The differential scattering cross section for the radiatively assisted collision (1) is

$$\frac{d\sigma_\omega}{d\Omega}(j,m\leftarrow j_0,m_0;\epsilon_0,q,\hat{k}_0,\hat{r})$$
$$=|f_\omega^+(j,m\leftarrow j_0,m_0;\epsilon_0,q,\hat{k}_0,\hat{r})|^2\ . \tag{9}$$

In order to obtain the basic cross sections which we need to describe the final-state distributions, we must integrate (9) over final scattering angles $\hat{r}$ and average over initial directions $\hat{k}_0$ and over the microcanonical distribution of m_0 states. This defines the integral cross section

$$\sigma_\omega(j,m\leftarrow j_0;\epsilon_0,q)$$
$$=\frac{1}{2j_0+1}\sum_{m_0=-j_0}^{j_0}\frac{1}{4\pi}\int|f_\omega|^2\sin\theta_k\sin\theta_r$$
$$\times d\theta_k d\theta_r d\phi_k d\phi_r\ , \tag{10}$$

where θ and ϕ represent the polar angles of $\hat{k}$ and $\hat{r}$.

Henceforth, we will simplify the notation and write the cross section (10) as

$$\sigma_\omega(j,m)\equiv\sigma_\omega(j,m\leftarrow j_0;\epsilon_0,q)\ , \tag{11}$$

where the indices j_0,ϵ_0,q are implied rather than written explicitly. We retain the subscript ω as a reminder that the cross section describes a radiatively assisted collision in which the photon participates. If we are not concerned about the distribution of m levels, but only about the total rate of production of state j, we need the cross sections defined by

$$\sigma_\omega(j)=\sum_{m=-j}^{j}\sigma_\omega(j,m)\ . \tag{12}$$

If we only want the total rate of photon absorption resulting from single collisions, we need the sum over all final states

$$\sigma_\omega=\sum_j\sigma_\omega(j)\ . \tag{13}$$

The quantities (11)—(13) are what we need in order to calculate the experimental observables discussed above.

The cross sections (11)—(13) depend on the intensity ϕ of the radiation field. We require ϕ to be sufficiently small that the effect of the radiation field on the nonradative scattering in the initial and final manifolds is negligible, and the probability of a radiatively assisted scattering event is much less than unity. These requirements ensure that the radiative scattering amplitude f_ω in (6) is linear in the dipole radiative coupling operator, and the cross sections (11)—(13) are linear in ϕ. This condition depends on the type of collision, and typical magnitudes are $\hbar\omega\phi \ll 10^9$ W cm^{-2} for a radiative collision and $\hbar\omega\phi \ll 10^6$ W cm^{-2} for wing absorptions in an optical collision.[12,26] In other words, it will always be satisfied for normal low-power laboratory experiments.

The radiation field interacts with the asymptotic A atom for an optical collision but not a radiative collision. Another way of saying this is that the molecular transition dipole moment of the AB molecule is nonvanishing as the internuclear separation $R\rightarrow\infty$ for the former, but vanishes as an inverse power of R for a radiative collision.[27] In order to eliminate any need to consider dressed atoms[12] and to justify the use of the field-free jm quantum numbers to describe the asymptotic atoms for optical collisions, we must also require that the detuning $\omega-\omega_0$ be much larger in magnitude than the Rabi frequency[12] Ω of the atom A. The problem of dressed atoms is discussed further in the Appendix . No such restriction on detuning is required for radiative collisions, since asymptotic radiative couplings are negligible.

For an optical collision we will also restrict the detuning to the wings of the profile where the absorption coefficient is proportional to (13). In addition to requiring $|\omega-\omega_\infty| \gg \Omega$, we must also require $|\omega-\omega_\infty| \gg \Delta\omega_{\max}$, where $\Delta\omega_{\max}$ is the largest of τ_r^{-1}, $\Delta\omega_D$, and $\Delta\omega_B$. Here τ_r is the natural radiative lifetime, $\Delta\omega_D$ is the Doppler width, and $\Delta\omega_B$ is the pressure-broadening width. We also assume the pressure is low enough that three-body effects can be ignored. With these restrictions, the rate of photon absorption, $K(\omega)\phi$, where $K(\omega)$ is the Beer's-law absorption coefficient (in units of length^{-1}), is equal to the conversion rate of reactants to products in (1), namely, $N_A N_B \langle \sigma_\omega v \rangle$. The average is over the Maxwellian distribution of velocity v and the distribution of initial states j_0. Thus the normalized absorption coefficient (in units of length^5) is

$$\frac{K(\omega)}{N_A N_B} = \frac{\langle \sigma_\omega v \rangle}{\phi} , \tag{14}$$

where N_A and N_B are the densities (in units of length^{-3}) of atoms A and B. Equation (14) applies to the whole profile for a radiative collision and to the wings for an optical collision. Since σ_ω is linear in laser power the normalized absorption coefficient is independent of ϕ, as it should be.

We also assume that any effects on the cross sections $\sigma_\omega(j,m)$ due to spontaneous emission can be neglected. This should be a good assumption since the spontaneous emission lifetime $\tau_r \gtrsim 10^{-9}$ sec will always be much longer than the time $\tau_c \approx 10^{-13}-10^{-12}$ sec during which a collision occurs. Of course, a proper account of spontaneous emission must be made if the experiment samples the long-time ($\sim\tau_r$) evolution of the atomic excited population following its creation by the rapid ($\sim\tau_c$) initial radiatively assisted collision. This is true if we are concerned with the depolarization due to hyperfine recoupling, weak external fields, or subsequent collisions (nonradiative) with other perturbers. Hyperfine and collisional depolarization will be discussed further in Sec. II G below. In the absence of nuclear spin or external fields, the polarization of the emitted light can be directly given in terms of the cross sections $\sigma_\omega(j,m)$ if the pressure is low enough that the time τ_d *between* depolarizing collisions is long compared to τ_r.

We give an example of typical magnitudes for some of these parameters for the Sr+Ar system with excitation of the Sr $5s5p\,{}^1P_1^o$ state from the ${}^1S_0$ ground state. The natural lifetime[28] corresponds to a broadening $\hbar\tau_r^{-1}=0.001$ cm^{-1}. The Rabi frequency corresponds to an energy $\hbar\Omega=0.004$ cm^{-1} for $\hbar\omega\phi=1$ W cm^{-2}, for which the probability of a radiatively assisted collision is on the order of 10^{-7} for a detuning $\hbar(\omega-\omega_\infty)$ of ± 10 cm^{-1}. Since the half-width at half maximum $\hbar\Delta\omega_B$ of the Sr pressure-broadened Lorentzian line core profile is 0.001 cm^{-1} for argon perturber densities of $\sim 4\times 10^{16}$ cm^{-3},[29] we may expect to achieve the low-pressure limit for pressures somewhat below 1 torr. At such pressures the absorption coefficient is given by (14) for detunings $|\omega-\omega_\infty| \gtrsim 1$ cm^{-1}. Note that we need not make any assumptions concerning $\omega-\omega_\infty$ relative to τ_c^{-1}. Equation (14) applies even in the "impact" region as long as $|\omega-\omega_\infty| \gg \Delta\omega_{\max}$. This can generally be satisfied at sufficiently low pressure and power.

B. Free-free states

We will set up a partial-wave expansion which enables us to make optimal use of molecular symmetries in calculating the radiative scattering cross sections (11)–(13). As in I, we will use the natural blocking of the field-free molecular Hamiltonian according to the conserved quantum numbers J, M, and p of the AB molecule. These characterize the total angular momentum, its space-fixed projection, and molecular parity, respectively. Molecular states for which at least one of these quantum numbers are different do not mix. Molecular states for which all three are the same mix due to coupling terms in the molecular Hamiltonian. The form of the coupling terms depends on the electronic-rotational basis set chosen. Although the molecular Hamiltonian may be approximately diagonal over some range of internuclear separation in one choice of basis, often corresponding to some idealized Hund's coupling case of angular momentum, the Hamiltonian will normally be strongly nondiagonal in this basis in some other range of internuclear separations. Thus a collision is often visualized as passing through several regions of R, each of which is approximately described by an idealized Hund's coupling case with the same J, M, and p.[16,17,30,31]

The quantum numbers which characterize the separated atomic fragments at large R are those for the electronic and nuclear rotation angular momenta, j and l, respectively. There is no interaction between j and l at large R. In order to construct the desired molecular states of total J and M, the states $|j,m\rangle\,|l,m_l\rangle$ with fixed-space projections of j and l must be coupled according to the rules of angular momentum addition, $\vec{J}=\vec{j}+\vec{l}$:

$$|j,l,J,M\rangle = \sum_{m,m_l} (j,l,J\,|\,m,m_l)\,|j,m\rangle\,|l,m_l\rangle \, . \tag{15}$$

The states (15), which correspond to a molecular Hund's case-(e) coupling scheme, define the channel states of scattering theory in terms of which the S matrix is given.[12,26,32,33]

The case-(e) states (15) have definite molecular parity[32]

$$p=(-1)^l p_A \, , \tag{16}$$

where p_A is the atomic parity of atom A. [Recall atom B has $j_B=0$. If $j_B\neq 0$, then j in (15) is replaced by $\vec{j}=\vec{j}_A+\vec{j}_B$ and p_A is replaced in (16) by $p_A p_B$.] Using (16), the parity of each $l=J+j,\ldots,|J-j|$ state for a given J can be specified according to the usual e and f designation of molecular parity:[34] an e state has parity $(-1)^J$ for integral J and parity $(-1)^{J-1/2}$ for half-integral J; an f state has the opposite parity of an e state for the same J. Table I gives the parities of possible l values for several different j's. Henceforth, the parity label p will be assumed to mean either e or f. (Please note that the parity label e has no connection with the Hund's case designation.)

The case-(e) states (15) diagonalize the asymptotic molecular Hamiltonian H^{AB}.[12,33] The asymptotic diagonal elements approach

$$H^{AB}(R) \rightarrow E_j^A + E^B + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{R^2} , \tag{17}$$

TABLE I. l values of each parity for a given j and J.

j	p_{AB}[a]	$p_A=+1$	$p_A=-1$
0	e	J	
	f		J
$\frac{1}{2}$	e	$J-\frac{1}{2}$	$J+\frac{1}{2}$
	f	$J+\frac{1}{2}$	$J-\frac{1}{2}$
1	e	J	$J-1$, $J+1$
	f	$J-1$, $J+1$	J
$\frac{3}{2}$	e	$J-\frac{1}{2}$, $J+\frac{3}{2}$	$J-\frac{3}{2}$, $J+\frac{1}{2}$
	f	$J-\frac{3}{2}$, $J+\frac{1}{2}$	$J-\frac{1}{2}$, $J+\frac{3}{2}$
2	e	$J-2$, J, $J+2$	$J-1$, $J+1$
	f	$J-1$, $J+2$	$J-2$, J, $J+2$

[a] e parity is $(-1)^J$ for integral J and $(-1)^{J-1/2}$ for half-integral J; f parity is opposite to e.

where the E's are the energies of the asymptotic atoms.

The R-dependent off-diagonal elements and corrections to the diagonal elements are, in general, proportional to the differences between molecular Born-Oppenheimer potential energy curves, that is, to R^{-6} in the case of van der Waals interaction between neutral atoms.[12] At small internuclear separations, the splittings between the molecular potentials become large compared to the splittings between the centrifugal potentials in (17) for different l. Thus, the molecular Hamiltonian is strongly nondiagonal in the case-(e) representation at small R, and switching to other molecular Hund's cases occurs. A detailed knowledge of the full molecular Hamiltonian is required to calculate the outcome of a nonradiative collision by which states of the same J, M, and p are mixed. The result of the collision is to induce transitions between case-(e) states of the same J, M, and p, but with different l. Such collisions are described by the scattering wave function

$$\Psi_c^+(j,l,J,M,p) = \sum_{j',l'} |j',l',J,M,p\rangle \times F_c^+(j',l'\leftarrow j,l;J,M,p;R)/R \ . \tag{18}$$

The radial functions F_c^+ are calculated from the standard close-coupled equations in the absence of a radiation field and take on the usual energy normalized form as $R\rightarrow\infty$,

$$F_c^+(j',l'\leftarrow j,l;J,M,p;R) \rightarrow i\left[\frac{\mu}{\hbar^2\pi}\right]^{1/2}[h_{jl}^-\delta_{jj'}\delta_{ll'}-h_{j'l'}^+S_c(j',l'\leftarrow j,l;J,p)] \ , \tag{19}$$

where

$$h_{jl}^{\pm}\rightarrow\frac{1}{(2k_j)^{1/2}}e^{\pm i(k_jR-\pi l/2)} \ . \tag{20}$$

The cross sections for collisional mixing of the atomic jm states $\sigma_c(j',m'\leftarrow j,m)$ can be given in terms of sums over the S_c matrix elements in (19); for example, a detailed treatment of ^2P fine-structure changing and depolarization cross sections has been given by Mies.[32]

C. Radiative coupling

The presence of a radiation field breaks the symmetry of the AB molecule. Therefore, a radiatively assisted collision causes a transition from an initial set of molecular states with quantum numbers J_0,M_0,p_0, to a final set of states with quantum numbers J,M,p. When the field is weak, only one photon can be exchanged between the field and molecule during a single collision, in accordance with the usual selection rules:

$$J=J_0+b \ , \tag{21}$$

$$M=M_0+q \ , \tag{22}$$

$$p=-p_0 \ . \tag{23}$$

In the language of molecular spectroscopy, transitions for which the branch index $b=-1,0,+1$ are, respectively, designated P,Q,R transitions for absorption and R,Q,P transitions for emission.

Our object is to calculate the S-matrix elements which describe the transition from a case-(e) state in the initial set of states to a case-(e) state in the final set of states. Since we assume the radiation field to be weak, the desired S-matrix element can be calculated in the distorted-wave Born approximation,[12,16,35] here called the radiative distorted-wave approximation (RDWA):

$$S_\omega(j,l,J,M,p\leftarrow j_0,l_0,J_0,M_0,p_0)=-2\pi i\langle\Psi_c^-(j,l,J,M,p)\,|\,V^{\text{rad}}\,|\,\Psi_c^+(j_0,l_0,J_0,M_0,p_0)\rangle \ . \tag{24}$$

Here Ψ_c^+ and Ψ_c^- are the scattering wave functions (18) which, respectively, describe the transitions among the initial channels and among the final channels in the absence of a radiation field, except that the final-state F_c^- function asymptotically approaches the complex conjugate of (19).[12]

The radiative coupling in (24) is[12]

$$V^{\text{rad}}=\left[\frac{2\pi\hbar\omega}{c}\phi\right]^{1/2}\hat{e}_q\cdot\vec{\text{d}} \ . \tag{25}$$

If the molecular dipole operator is expanded in spherical tensor form

$$\vec{\text{d}}=\sum_{i=-1}^{1}\hat{e}_i^*d_i^{(1)} \ , \tag{26}$$

then

$$\hat{e}_q\cdot\vec{\text{d}}=d_q^{(1)} \ . \tag{27}$$

Our object is to calculate S_ω from close-coupled equations including the radiation field. Since the RDWA (24) shows that S_ω depends linearly on the V^{rad} operator, we may use the Wigner-Eckart theorem[36] to *factor* S_ω into a geometrical and dynamical part

$$S_\omega(j,l,J,M,p\leftarrow j_0,l_0,J_0,M_0,p_0) \\ =(J,1,J_0\,|\,M,-q)s_\omega^b(j,l\leftarrow j_0,l_0;J_0,p_0)\ . \quad (28)$$

The reduced radiative S-matrix elements s_ω^b contain all the dynamical information about the radiatively assisted collision and are labeled according to the state-to-state case-(e) transitions $j,l\leftarrow j_0,l_0$ possible for each transition branch b from states of each initial J_0 and parity. The particular definition (28) corresponds to that used in I, chosen for convenience in carrying out summations.

The factorization (28), based on the assumption of a sufficiently weak radiation field, is a very powerful tool for simplifying our results. For strong fields S_ω will generally depend nonlinearly on V^{rad}, and separate dynamical calculations are required for each M.[37] However, the factorization (28) permits us to set up the coupled equations for radiative scattering which are independent of M, just as the coupled equations for nonradiative scattering are independent of M. All geometric effects are incorporated in angular momentum algebra and all dynamical effects are contained in the reduced matrix elements s_ω in the Hund's case-(e) representation. The s_ω may be calculated directly by a close-coupled scattering calculation using reduced radiative coupling matrix elements in the Hamiltonian

$$(j,l,J\,||d^{(1)}||\,j_0,l_0,J_0)=\frac{\langle j,l,J,M\,|\,d_q^{(1)}\,|\,j_0,l_0,J_0,M_0\rangle}{(J,1,J_0\,|\,M,-q)}\ . \quad (29)$$

The M-independent molecular Hamiltonian which defines the set of close-coupled equations which we must solve takes on the following matrix structure:

$$\begin{bmatrix} [\{j_0l_0\}J_0p_0]_{n_0\times n_0} & [\{j_0l_0\}J_0p_0\rightarrow\{jl\}Jp]_{n_0\times n} \\ [\{jl\}Jp\leftarrow\{j_0l_0\}J_0p_0]_{n\times n_0} & [\{jl\}Jp]_{n\times n} \end{bmatrix}\ . \quad (30)$$

We assume a manifold of n_0 initial states and n final states. The quantities in curly brackets in (30) show the quantum numbers of the electronic-rotational basis, here shown for case (e). Other Hund's cases with different quantum numbers than $\{jl\}$ could also be used, so long as the asymptotic solutions are projected on a case-(e) basis; for example, Hund's case (a) was used in I to formulate the coupled equations.

For each initial J_0p_0 manifold, there are three possible final-state blocks corresponding to the transition branches $b=J-J_0=0,\pm1$. Unless the initial state is nondegenerate there will be two possible parities $p_0=e$ or f associated with each initial J_0. Therefore, for each value of initial-state total angular momentum J_0, there are six *sets* of coupled equations (30) (only three sets for nondegenerate initial states, $j_0=0$).

D. Case-(e) reduced dipole matrix elements

The off-diagonal $n_0\times n$ or $n\times n_0$ dipole coupling matrix in (30) contains the terms responsible for the radiative coupling. These matrix elements were explicitly worked out in I for a collision-induced ${}^1D\leftarrow{}^1S$ transition. We will here obtain the general Hund's case-(e) selection rules for optical and radiative collisions. The specific ${}^1P$-${}^1S$ case has already been presented.[12] From the standpoint of our coupled equation molecular formulation, the only place where the difference between an optical and radiative collision occurs is in the asymptotic form of the dipole coupling matrix elements: these approach R-independent constants for the former and vary as an inverse power of R for the latter.[12,27] This difference in R-dependent radiative coupling leads to dramatic differences in the frequency dependence of the cross section $\sigma_\omega(j)$ for small detuning in the impact region of the profile, $|\omega-\omega_\infty|\lesssim\tau_c^{-1}$. These differences have been briefly discussed before,[17] and will be treated more fully in a future paper.

For an optical collision the asymptotic reduced matrix elements can be written down immediately if we ignore their negligibly small R variation since the space-fixed dipole operator $d_q^{(1)}$ does not depend on the coordinates occurring in the spherical harmonics Y_{lm} describing the eigenstates of nuclear angular momentum. Using Eq. (6.25) of Rose[36] and the definition (29), we find for an optical collision

$$(j,l,J\,||d^{(1)}||\,j_0,l_0,J_0) \\ =\delta_{ll_0}(-1)^{l_0+b-j_0-J_0}(2j+1)^{1/2}(2J+1)^{1/2} \\ \times W(j_0,j,J_0,J;1,l)(j\,||d^{(1)}||\,j_0)\ . \quad (31)$$

The reduced atomic matrix element for atom A, $(j\,||d^{(1)}||\,j_0)$, satisfies

$$\sum_{m_0,q}|\langle j,m\,|\,d_q^{(1)}\,|\,j_0,m_0\rangle|^2=(2j+1)(j\,||d^{(1)}||\,j_0)^2 \\ =(2j_0+1)(j_0\,||d^{(1)}||\,j)^2\ , \quad (32)$$

and can be found from the measured oscillator strength of the $j\leftarrow j_0$ transition.

Equation (31) embodies the selection rule for optical collision reduced dipole matrix elements, $\Delta l=0$; that is, if a radiative transition occurs at large internuclear separations, only the electronic angular momentum of atom A changes, not the nuclear rotation angular momentum. Note that this selection rule applies *only* to the $d^{(1)}$ coupling operators, *not* to the s_ω matrix elements, since inelastic couplings among case-(e) states can result in $\Delta l\neq0$ transitions (parity considerations ensure that Δl changes must be even). However, in the *absence* of inelastic couplings, only $\Delta l=0$ transitions can occur in an optical collision.

Calculation of the reduced transition dipole for radiative collisions depends on the existence of the interatomic interactions $V^{AB}(R)$.[10,27] We must introduce the effect of V^{AB} on the asymptotic atomic wave function in order to find the matrix elements. Let us introduce the R dependence through first order in V^{AB} (Refs. 38 and 39)

$$|\,j,m;R\,\rangle=[1+G_{jm}^{AB}V^{AB}(R)]\,|\,j,m\,\rangle\ , \quad (33)$$

where $|j,m\rangle$ represents the asymptotic product state

$$|j,m\rangle = |A(j,m)\rangle\,|B\rangle\ , \tag{34}$$

and G^{AB} is the resolvent involving summation over all products states of atoms A and$B$ other than those in (34). The reduced radiative matrix elements thus depend on the matrix elements of the type (here integrating only over atomic coordinates for fixed R)

$$\langle A(j,m)B\,|\,V^{AB}G^{AB}_{jm}d_q^{(1)}+d_q^{(1)}G^{AB}_{j_0m_0}V^{AB}\,|\,A(j_0,m_0)B_0\rangle\ . \tag{35}$$

If the usual expansion of V^{AB} in multipole interactions is made, the lead term in the R-dependent transition dipole can be found. Recall that V^{AB} contains terms $Y^L_M Y^{L'}_{-M}$ for the L-pole—L'-pole interaction. These are expressed relative to quantization on the internuclear axis $\vec{R}$. In order to integrate over the coordinates of the axis, it is necessary to rotate these Y's into Y's defined in the space-fixed axis system. This introduces products of rotation matrices $D^L D^{L'}$ in the integral and leads to the selection rules on l.

If the product of atomic parities $p_A p_B$ is different for the initial and final states, the lead term in the multipole expansion of V^{AB} is the dipole-dipole term, $L=L'=1$, varying as R^{-3}.[27] In this case, we obtain the selection rule $l=l_0,l_0\pm 2$. If the product of atomic parities is the same for initial and final states, the lead term is the dipole-quadrupole term, $L=1,L'=2$, varying as R^{-4}.[27] In this case, we obtain the selection rule $l=l_0\pm 1,l_0\pm 3$. A detailed example of this case is worked out in I. Thus we see that for radiative collisions, direct radiative transitions with $\Delta l\neq 0$ are possible. These can occur even in the absence of inelastic collisional mixing of states, since the transition moments are of longer range (R^{-3} or R^{-4}) than the R^{-6} interatomic interactions responsible for inelastic collisions. The effect of $\Delta l\neq 0$ transitions on the radiative collision profiles can be significant. Numerical calculations have demonstrated the splitting apart of P, Q, and R contributions to the total line profile due to $\Delta l\neq 0$ transitions.[16,17]

E. Cross sections

Standard scattering theory techniques allow us to write the desired radiative scattering amplitudes (9) in terms of the S-matrix elements found by solving the coupled scattering equations:

$$f_\omega^{+}(j,m\leftarrow j_0,m_0;\epsilon_0,q,\hat{k}_0,\hat{r}) = \frac{2\pi i}{k_0}\sum_{l_0,l,m} i^{\,l_0-l}\,Y^{l_0*}_{M_0-m_0}(\theta_k,\phi_k)\,Y^l_{M-m}(\theta_r,\phi_r) \times g_\omega(j,l,M,m\leftarrow j_0,l_0,M_0,m_0;\epsilon_0,q)\ , \tag{36}$$

where the Y's are spherical harmonics and

$$g_\omega(j,l,M,m,\leftarrow j_0,l_0,M_0,m_0;\epsilon_0,q) = \sum_{J_0,J}(l_0,j_0,J_0\,|\,M_0-m_0,m_0)(l,j,J\,|\,M-m,m) \times S_\omega(j,l,J,M,p\leftarrow j_0,l_0,J_0,M_0,p_0;\epsilon_0,q)\ . \tag{37}$$

When we average over initial states and integrate over final scattering angles as in (10), we find that the cross sections (11) are

$$\sigma_\omega(j,m) = \frac{\pi}{k_0^2}\sum_{l_0,l,J_0,M_0}|\,h_\omega(j,l,m\leftarrow j_0,l_0,J_0,M_0;\epsilon_0,q)\,|^2\ , \tag{38}$$

where

$$h_\omega(j,l,m\leftarrow j_0,l_0,J_0,M_0;\epsilon_0,q) = \sum_J (l,j,J\,|\,M-m,m) \times S_\omega(j,l,J,M,p\leftarrow j_0,l_0,J_0,M_0,p_0;\epsilon_0,q)\ . \tag{39}$$

The expression (38) can be greatly simplified by making use of the single dynamical assumption which we make concerning the weakness of the radiation field. If we now introduce the factorization (28) into (39), the summation over M_0 can now be explicitly carried out after introducing the equality

$$(J,1,J_0\,|\,M,-q)(l,j,J\,|\,M-m,m) = \sum_{t=j-1}^{j+1}(2J+1)(2t+1)(j,1,t\,|\,M,-q)(l,t,J_0\,|\,M-m,m-q)\,W(l,j,J_0,1;J,t)\ , \tag{40}$$

where W is a Racah coefficient.

We find the cross sections (11) are

$$\sigma_\omega(j,m) = \sum_{t=j-1}^{j+1}\frac{3(j,1,t\,|\,m,-q)^2}{2t+1}\sigma^t_\omega(j)\ , \tag{41}$$

where the transfer cross sections σ^t are defined by

$$\sigma^t_\omega(j) = \frac{\pi}{k_0^2}\sum_{J_0}\frac{2J_0+1}{3}\sum_{l,l_0}|\,p^t_\omega(j,l\leftarrow j_0,l_0;J_0,p_0,\epsilon_0)\,|^2 \tag{42}$$

with

$$p^t_\omega(j,l\leftarrow j_0,l_0;J_0,p_0,\epsilon_0) = \sum_{b=-1}^{+1}(2J+1)^{1/2}(2t+1)^{1/2}W(l,j,J_0,1;J,t) \times s^b_\omega(j,l\leftarrow j_0,l_0;J_0,p_0,\epsilon_0) \tag{43}$$

and $J=J_0+b$. Note that the parity label p_0 in p^t_ω is redundant, since it is given by Eq. (16) once l_0 is known. We include it to indicate that for nondegenerate initial states, $j_0\neq 0$, the sum in (42) can be broken down into two components, one for e and one for f initial parity:

$$\sigma^t_\omega(j)=\sigma^t_\omega(j,e)+\sigma^t_\omega(j,f)\ . \tag{44}$$

The expressions (41)–(43) define the cross sections necessary to describe the orientation and alignment of the A atom following a radiatively assisted collision. Equations (41)–(43) have the same structure as the expressions which have been developed to describe fragment polarization following photofragmentation.[23–25] This similar structure is merely a consequence of two common features of both theories: (a) the factorization (28), which leads to the irreducible tensor expansion in Eq. (40), due to the perturbative nature of radiative coupling, and (b) the averaging over an isotropic distribution of initial states. The expression (41) is useful in that it separates geometrical and dynamical effects in the total cross sections $\sigma_\omega(j,m)$. The complete dependence on the geometric quantum numbers m and q is contained in the Clebsch-Gordan coefficients $(j,1,t\mid m,-q)$. All dynamical information is contained in the transfer cross sections σ^t. Clearly, $t=j,j\pm1$ has only three possible values. We use the nomenclature transfer cross section for σ^t following the interpretation of t by Greene and Zare[24,25] as the angular momentum transferred from the photon to all final-state angular momenta other than that j of the atom observed.

The transfer cross sections σ^t depend on initial kinetic energy and photon frequency ω through the reduced radiative S-matrix elements $s^b_\omega(j,l\leftarrow j_0,l_0;J_0,p_0,\epsilon_0)$ in the Hund's case-(e) representation. These give the smallest number of dynamically independent amplitudes which we must calculate in order to calculate the cross sections σ^t. Note that the σ^t depend on *coherent* sums of these amplitudes. Each such sum contains one s^b_ω from each of the three possible molecular transition branches b that occur by a radiative transition from an initial j_0l_0 state with total angular momentum J_0. Since final states of different b for the same initial J_0l_0 necessarily have different total angular momentum J, and since molecular states of different J do not interact (we neglect very weak second-order interactions through the radiation field), the σ^t depend on the independent dynamical evolution of the coherent mixture of molecular states prepared by photon absorption in the three different branches b.

The total cross section $\sigma_\omega(j)$ for producing the final state j irrespective of m can be readily found from (12) and (41). The summation over m can be trivially carried out:

$$\sigma_\omega(j)=\sum_{t=j-1}^{j+1}\sigma^t_\omega(j)\ . \tag{45}$$

Furthermore, the coherent sums in (43) can be eliminated by explicitly carrying out the summation over t, since t occurs only in the Racah coefficient. Thus we may also write

$$\sigma_\omega(j)=\sum_{b=-1}^{+1}\sigma^b_\omega(j)\ , \tag{46}$$

where the branch cross sections σ^b are defined by

$$\sigma^b_\omega(j)=\frac{\pi}{k_0^2}\sum_{J_0}\frac{2J_0+1}{3}\sum_{l_0,l}\left|s^b_\omega(j,l\leftarrow j_0,l_0;J_0,p_0,\epsilon_0)\right|^2\ . \tag{47}$$

We see that the cross section $\sigma_\omega(j)$ can be separated into a sum of partial cross sections in either of two ways, (45) or (46). The calculation of transfer partial cross sections is the natural choice if the goal is also to calculate product polarization. However, calculation of branch partial cross sections provides a simpler summation if we are not concerned with product polarization, as is the case in I and Ref. 18. The sum in (47) requires only an incoherent summation of s^b_ω matrix elements from the *same* branch and does not require that we first calculate the coherent sums (43). The branch cross sections σ^b thus are found from sums which result from the natural symmetry blocking (30) of the molecular Hamiltonian that is used to calculate the molecular dynamics. Although interference between *different* branches is eliminated in (47), the individual s^b_ω matrix elements may exhibit interference effects if the same final state jl can be reached from the same initial state j_0l_0 by more than one path in the overall branch Hamiltonian.

In general, we may expect the partial branch cross section σ^b_ω to be different for different values of branch index b, since the dynamics occurs with different Hamiltonians (30). These differences have been observed, especially in the core and near-wing regions of the profile, for both optical and radiative collisions for all of the systems for which we have carried out numerical calculations so far.[16,17,19] If the initial state is degenerate, $j_0\neq0$, the branch cross section can also be broken down into separate contributions from e and f initial parity states, just as for σ^t in (44).

F. Orientation and alignment

The above theory for the cross sections describes the distribution of excited atomic jm states which results from a radiatively assisted collision. We wish to use these to predict the results of experiments which probe this distribution by measuring the properties of the atomic fluorescence from the manifold of jm states to a manifold of final states j_fm_f (which may be the initial state j_0 of A). We assume that the fluorescence intensity over the whole spectral profile of atom A is detected, so that we must sum the contributions of all m and m_f sublevels. We assume that the emission frequency in the vicinity of ω_f is sufficiently different from the excitation frequency ω that the atomic fluorescence is resolved from the Rayleigh scattered light at frequency ω.

A complete theory of the spatial distribution and polarization of the fluorescence has been developed by Fano and Macek.[40] This theory has recently been reviewed and applied to photofragmentation problems (i.e., photoionization and molecular photodissociation) by Greene and Zare.[25] This theory applies directly to the present problem. The reader is referred to Greene and Zare's excellent article for full details. We will briefly summarize here the main results as they apply to radiatively assisted collisions.

The intensity $I(\phi,\theta,\chi)$ of light measured by a detector having polar coordinates (θ,ϕ) relative to the emission region and polarization analyzer axis oriented at angle χ is (again, refer to Greene and Zare[25] for full definitions)

$$I(\phi,\theta,\chi)=\frac{I_0}{3}\{1-h^{(2)}(j,j_f)\mathscr{A}_0[P_2(\cos\theta)-\tfrac{3}{4}\sin^2\theta\cos(2\chi)\cos(2\beta)]+\tfrac{3}{2}h^{(1)}(j,j_f)\mathscr{O}_0\cos\theta\sin(2\beta)\} . \tag{48}$$

The angle β specifies the nature of the polarization vector of the detected light: $\beta=0$ for linear polarization and $\beta=\pm\pi/4$ for left and right circular polarization. The factors $h^{(1)}$ and $h^{(2)}$ are purely geometric quantities tabulated by Greene and Zare. All information about the distribution of jm states is contained in the orientation and alignment parameters, $\mathscr{O}_0$ and $\mathscr{A}_0$, respectively. These may be expressed in terms of our cross sections (41) and (45) as

$$\mathscr{O}_0(j,\omega)=\sum_{m=-j}^{j}\frac{m}{\sqrt{j(j+1)}}\frac{\langle\sigma_\omega(j,m)v\rangle}{\langle\sigma_\omega(j)v\rangle} , \tag{49}$$

$$\mathscr{A}_0(j,\omega)=\sum_{m=-j}^{j}\left[\frac{3m^2}{j(j+1)}-1\right]\frac{\langle\sigma_\omega(j,m)v\rangle}{\langle\sigma_\omega(j)v\rangle} . \tag{50}$$

The average is over the distribution of velocities v and initial states j_0.

Orientation can only be created by excitation with left or right circularly polarized light, whereas alignment can be created by circularly polarized, linearly polarized, or unpolarized (equal mixtures of left and right circularly polarized) light. Furthermore, orientation is measured by circularly polarized detection, whereas alignment is measured by linearly polarized detection.

The excitation-detection geometry in the recent optical[4–7] and radiative[11] collision polarization experiments has been very simple: excitation by linearly polarized light followed by measurement of the parallel, $I_{\parallel}=I(\phi,\pi/2,\chi=0)$, and perpendicular, $I_{\perp}=I(\phi,\pi/2,\chi=\pi/2)$, linearly polarized fluorescence intensities with a detector in a plane perpendicular to the polarization vector $\hat{e}_0$ of the exciting light. These experiments, which only measure alignment, define a polarization ratio as a function of excitation frequency. Two definitions of this ratio may be used. It may be defined as a normalized Stokes parameter[41]

$$P_S(\omega)=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}} , \tag{51}$$

or it may be defined as the longitudinal polarization[5]

$$P_L(\omega)=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+2I_{\perp}} . \tag{52}$$

These two are related by

$$P_L=\frac{2P_S}{3-P_S} , \tag{53}$$

and both may be expressed solely in terms of the alignment parameter

$$P_S=\frac{3h^{(2)}(j,j_f)\mathscr{A}_0}{4+h^{(2)}(j,j_f)\mathscr{A}_0} , \tag{54}$$

$$P_L=\tfrac{1}{2}h^{(2)}(j,j_f)\mathscr{A}_0 . \tag{55}$$

The alignment parameter is directly proportional to the measured P_L. The geometric factor $h^{(2)}$ has the values $-j/(2j+3)$, 1, and $-(j+1)/(2j-1)$ for the respective values $j_f=j+1$, j, and $j-1$.

If we insert Eq. (41) into (50), the dynamic alignment parameter can readily be expressed in terms of the transfer cross sections σ^t and universal geometric functions $G_0^t(j)$:

$$\mathscr{A}_0=\frac{\sum_t \sigma_\omega^t(j)G_0^t(j)}{\sum_t \sigma_\omega^t(j)} . \tag{56}$$

A similar expression applies for $\mathscr{O}_0$. General expressions for these geometric functions for orientation and alignment are tabulated by Greene and Zare for both linear and circularly polarized excitation. The specific results for alignment induced by linear polarization are

$$G_0^t(j)=\begin{cases}-\dfrac{2}{5}-\dfrac{3}{5j} & \text{for } t=j-1\\[2mm] \dfrac{4}{5}-\dfrac{3}{5j(j+1)} & \text{for } t=j\\[2mm] -\dfrac{2}{5}+\dfrac{3}{5(j+1)} & \text{for } t=j+1 .\end{cases} \tag{57}$$

G. Additional depolarization effects

The theory we have developed describes the polarization of fluorescence due to the distribution of electronic jm states created by a single radiatively assisted collision. Often other interactions may be present which modify this polarization. These could be hyperfine recoupling with nuclear spin I following the initial electronic excitation, precession caused by an external magnetic field, or population changes due to subsequent inelastic collisions. The time scale τ_c associated with the initial radiatively assisted collision is much smaller than that of the fluorescence τ_r. If the time scale associated with one of these additional effects is τ_d, the effect can be ignored only if $\tau_d \gg \tau_r$.

In general, our cross-section results must be embedded in a more general theory which takes into account these other interactions. We may think of the very rapid radiatively assisted collision as preparing an excited-state electronic density matrix $\rho(j,m;j',m')$ at time $t=0$, which then subsequently evolves in time under the influence of these other effects. In our problem of radiative redistribution only the diagonal electronic density-matrix elements are needed. These are proportional to the cross sections

$\sigma_\omega(j,m)$. We can, of course, expand either ρ or σ in the usual irreducible spherical tensor form[42]

$$\sigma_\omega(j,m)=\sum_k(-1)^{m-j}(j,j,k\mid m,-m)\sigma_\omega^{(k)}(j)\ , \tag{58}$$

where the initially created population, orientation $\mathscr{O}_0$, and alignment $\mathscr{A}_0$ are, respectively, proportional to $\sigma^{(0)}$, $\sigma^{(1)}$, and $\sigma^{(2)}$. The time evolution can be calculated using either standard density-matrix techniques or other alternatives.

The role of hyperfine recoupling has been treated by Fano and Macek.[40] Completely equivalent results can be obtained using our time-independent scattering wave function following the method of Percival and Seaton.[43] The results of the Fano-Macek theory have been summarized by Greene and Zare.[25] The observed orientation and alignment parameters $\mathscr{O}$ and $\mathscr{A}$ are proportional to the electronic parameters of Eqs. (49) and (50):

$$\mathscr{O}=g^{(1)}\mathscr{O}_0\ , \tag{59}$$

$$\mathscr{A}=g^{(2)}\mathscr{A}_0\ . \tag{60}$$

The proportionality constants $0\le g^{(k)}\le 1$ incorporate the depolarizing effect of precession of $\vec{\mathrm{j}}$ induced by hyperfine coupling of $\vec{\mathrm{I}}$ and $\vec{\mathrm{j}}$:

$$g^{(k)}=\sum_{F,F'}\frac{(2F+1)(2F'+1)}{2I+1}\begin{Bmatrix}F & F' & k\\ j & j & I\end{Bmatrix}^2\frac{1}{1+\omega_{FF'}^2\tau_r^2}\ . \tag{61}$$

The index $k=1$ for orientation and 2 for alignment. Since we assume that the fluorescence in all hyperfine lines is detected, the summation in (61) runs over all excited state F and F' consistent with $\vec{\mathrm{F}}=\vec{\mathrm{j}}+\vec{\mathrm{I}}$. The hyperfine splitting between levels F and F' is $\hbar\omega_{FF'}$. If all splittings $\omega_{FF'}$ are much less than τ_r^{-1}, then $g^{(k)}\approx 1$ and hyperfine effects can be ignored.

The theory developed so far in this paper applies to the low-pressure limit of the polarization ratio, when no depolarization due to perturber collisions occurs before emission. The general situation calls for solving the density matrix equations which describe production of orientation and alignment by radiatively assisted collisions and loss by depolarization collisions.[20,21] Note that our close-coupling formulation gives not only the radiative scattering S_ω matrix elements, but also the S_c matrix elements that describe elastic and inelastic collisions of the final-state jm A atom with perturber B. The necessary cross sections can be calculated from the S_c matrix using standard techniques. Therefore, the radiative scattering close-coupling calculation produces both the radiative σ_ω and nonradiative σ_c collision cross sections and enables us to give a complete description of the polarization ratio, including its pressure dependence.

The calculation of the pressure dependence of P_L will be illustrated here for the simplest possible case, namely, $j_0=0$ and $j=1$ with no nuclear spin. This case corresponds to the group-II-metal—rare-gas systems which have been studied experimentally.[4–7] The only depolarizing cross sections $\sigma_c(j,m\leftarrow j,m')$ needed in this case are $\sigma_c(0,1)$ and $\sigma_c(1,-1)$ (m values only are given). It is a straightforward matter to set up the kinetic rate equations which give the steady-state populations of the excited levels. If we expand the radiative cross sections and excited-state densities in the usual irreducible tensor components, Eq. (58), then the kinetic equation for the kth multipole is

$$\dot{\rho}^{(k)}=\langle\sigma_\omega^{(k)}v\rangle N_AN_B-(\tau_r^{-1}+\gamma_c^{(k)})\rho^{(k)}\ , \tag{62}$$

where $k=0$, 1, or 2, and

$$\gamma_c^{(0)}=0\ , \tag{63}$$

$$\gamma_c^{(1)}=\langle[\sigma_c(0,1)+2\sigma_c(1,-1)]v\rangle N_B\ , \tag{64}$$

$$\gamma_c^{(2)}=3\langle\sigma_c(0,1)v\rangle N_B\ , \tag{65}$$

represent destruction rates of population, orientation, and alignment, respectively. The population destruction rate $\gamma_c^{(0)}$ vanishes since we assume no inelastic quenching.

The steady-state solution to (62) gives

$$\rho^{(k)}=\langle\sigma_\omega^{(k)}v\rangle N_AN_B\tau_r\frac{1}{1+\gamma_c^{(2)}\tau_r}\ . \tag{66}$$

The polarization ratio is

$$P_L=-\mathscr{A}_0\frac{1}{1+\gamma_c^{(2)}\tau_r}\ , \tag{67}$$

where $\mathscr{A}_0$ is the zero-pressure limit of the alignment parameter given by (50). The expression (67) is equivalent to that used by Alford *et al.*[5] to extract $P_S(N_B=0)$ and $\gamma_c^{(2)}$ from the pressure dependence of their measured polarization ratios: $1/P_L$ is linear in the perturber pressure by virtue of (65). Alford *et al.* were thus able to obtain $\gamma_c^{(2)}/N_B$ from their measured slope and the known value of τ_r.

The pressure dependence of the orientation parameter is given by a similar expression:

$$\mathscr{O}_0(N_B)=\mathscr{O}_0(N_B=0)\frac{1}{1+\gamma_c^{(1)}\tau_r}\ . \tag{68}$$

We see that measurement of the pressure dependence of the orientation parameter in a circularly polarized excitation-detection experiment can be used to extract the $\langle\sigma_c(1,-1)v\rangle$ rate coefficient if $\langle\sigma(0,1)v\rangle$ is known from an alignment experiment. An approach similar to the above for a $j=1$ atom may be set up for more complex atoms. In general, both hyperfine and collisional depolarization would have to be accounted for.

III. CONCLUSION

If our goal is to calculate the experimental observables in a radiatively assisted collision using our close-coupled formulation, then we must be able to calculate the case-(e) reduced matrix elements s_ω. These determine the differential scattering amplitudes f_ω^{+} in terms of which various observables can be expressed. The f_ω^{+} can be used to determine not only the cross sections $\sigma_\omega(j,m)$ but also the angular distributions of final-state products or even the results of coincidence experiments. As long as the radiation field is sufficiently weak—and this covers the great majority of laboratory experiments and applications—the

s_ω remain linear in the radiative coupling operator. This permits the key factorization (28). The effect of the radiation is to introduce weak perturbative transitions in the colliding system but otherwise does not perturb the field-free collision dynamics.

If the trivial multiplicative factors in s_ω are factored as in I, then reduced free-free dipole matrix elements d_ω^{ff} can be defined[16] which depend only on the properties of the AB molecule:

$$s_\omega = -2\pi i \left[\frac{2\pi\hbar\omega}{c} \phi \right]^{1/2} d_\omega^{\text{ff}} \ . \tag{69}$$

We see from (24) and (28) that these matrix elements

$$d_\omega^{\text{ff}} = (\Psi_c^- || d^{(1)} || \Psi_c^+) \tag{70}$$

are analogous to the adiabatic dipole free-free Franck-Condon amplitudes of conventional line-broadening theory, but contain additional information in the scattering wave functions $\Psi_c^\pm$ about inelastic collisions in the initial and final states.[12] We may think of them as generalized nonadiabatic free-free dipole Franck-Condon amplitudes.

In view of (69) the relation of our radiatively assisted collision theory to photofragmentation theory becomes even more intimate than implied by symmetry considerations. The photofragmentation transition amplitudes, for which radiation is also treated as a perturbation, are expressed in terms of bound-free dipole amplitudes

$$d_\omega^{\text{bf}} = (\Psi_c^- || d^{(1)} || \Psi_b) \ , \tag{71}$$

where the initial state Ψ_b is a bound state instead of a scattering state. Both radiatively assisted collisions and photofragmentation sample final-state interactions implicit in the final-state scattering wave function Ψ_c^-. Our close-coupled theory of radiatively assisted collisions is essentially equivalent in its ability to treat final-state interactions to the recently developed driven equation formulation of molecular photodissociation.[44] The two phenomena differ, of course, in the role of the initial state. Photodissociation offers the possibility of experimentally choosing particular J_0 values through judicious preparation of the initial bound state, whereas radiatively assisted collisions always select a wide range of incoming partial waves.

The next paper of this series will develop explicitly a half-collision viewpoint of radiatively assisted collisions that is analogous to the half-collision viewpoint of photodissociation.[22,44] The separation of initial- and final-state dynamics contained in the RDWA (24) permits us to look at a radiatively assisted collision as a sequence of two half-collisions, one in the initial manifold of states and one in the final manifold. The generalized multichannel quantum defect analysis (MCQDA) of scattering wave functions in arbitrary potentials[45–47] provides a powerful tool in this regard. The MCQDA not only enables us to relate the initial-state scattering Ψ^+ and bound Ψ_b wave functions by analytic continuation across the initial-state dissociation threshold, but also permits us under suitable conditions to factor the matrix of d_ω^{ff} into separate matrices that describe initial-state dynamics, adiabatic Franck-Condon radiative excitation, and final-state dynamics.[17] In this manner we will show that our close-coupled polarization ratio P_L for far-wing excitation in the group-II—rare-gas systems can be reduced through the WKB approximation to a form equivalent to that found by Lewis *et al.*[48] on the basis of a simple geometric model. Furthermore, the same theory of final-state interactions applies to a recent photodissociation experiment and leads to a similar interpretation.[49,50]

APPENDIX

We will here consider some of the problems associated with the presence of asymptotic radiative couplings, which always occur for optical collisions. No problem occurs for radiative collisions, since the dipole coupling operators decrease asymptotically as R^{-n}, $n \geq 3$.

The case-(e) states describe field-free atoms. When the field is present and tuned near an atomic transition frequency, $\omega \approx \omega_\infty$, the upper and lower atomic states of definite angular momentum are mixed, and j, j_0 are no longer good quantum numbers. The mixing does not affect the l quantum numbers, as shown by the $\Delta l = 0$ selection rule in (31). Thus, when we set up the electronic-rotational-radiation Hamiltonian matrix H in the form (30), only states of the same $l = l_0$ are coupled, i.e., for each initial l_0 and branch b, there is only one possible upper jlJ state with $l = l_0$ that can couple radiatively to the lower $j_0 l_0 J_0$ state.

The dressed representation is found by diagonalizing the asymptotic Hamiltonian of (30),

$$\underline{H}_d = \underline{U}\underline{H}\underline{\tilde{U}} \ , \tag{A1}$$

$$|\underline{d}\rangle = \underline{U}|\underline{e}\rangle \ , \tag{A2}$$

where $|\underline{d}\rangle$ and $|\underline{e}\rangle$ represent the respective column vectors of dressed and case-(e) electronic-rotational-radiation basis functions. If

$$\frac{\Omega}{|\omega - \omega_\infty|} \ll 1 \ , \tag{A3}$$

where Ω is the atomic Rabi frequency,[12] then by perturbation theory the terms in U associated with the dressing of the asymptotic atoms are of the order of $\Omega / |\omega - \omega_\infty|$. Therefore, if the s_ω are calculated in the dressed representation (A2), they will differ from those in the (e) representation by terms on the order of $\Omega / |\omega - \omega_\infty|$. We thus avoid any problems associated with asymptotic radiative couplings by requiring that (A3) be satisfied.

The above discussion applies when we set up the coupled equations considering only one final-state branch at a time in Eq. (30). We encounter a different set of problems when *all* final-state branches are included in the *same* set of coupled equations. This method expands the set of equations (30) so as to permit calculation of all matrix elements at the same time, and was utilized for the Sr+Ar system in Ref. 17. We will use this case as an example. There are six coupled equations, and states of the same $l = l_0$ are present in each of the P, Q, and R final-state blocks for the different transition branches. These three final states of the same l are completely degenerate in the electronic-rotational-radiative Hamiltonian at sufficiently large R that the R^{-6} long-range molecular potentials have damped to negligible values [see Eq. (17)]. The presence of the asymptotic radiation field mixes the three excited ^1P case-(e) states of the same l (but different J) to give dressed excited states (we consider here only that part of the dressing that affects these degenerate excited states and ignore terms of order $\Omega/|\omega-\omega_\infty|$),

$$\underline{d}^l=\underline{U}^l(3\times3)\underline{e}^l\,, \tag{A4}$$

where $\underline{e}$ and $\underline{d}$ are three-element column vectors. The elements of $\underline{U}$ are all of comparable magnitude, say on the order of $3^{-1/2}$.

One of the three dressed states resulting from the diagonalization (A4) is nondegenerate, corresponding to the $m=0$ state which couples radiatively to the ground state for linear polarization. Its row in the unitary matrix $\underline{U}$ is symmetry determined. The other two dressed states remain degenerate, corresponding to the two $m=\pm1$ states which do not couple radiatively to the ground state. The eigenvectors of these twofold degenerate states are not unique, but have an arbitrary rotation among themselves depending on the actual numerical algorithm used to diagonalize the asymptotic Hamiltonian.

In order to generate $s_\omega(e)$ matrix elements in the case-(e) representation when they are calculated in the asymptotically diagonal dressed representation, $s_\omega(d)$, it is necessary to rotate the vector of three dressed matrix elements of the same l back to the case-(e) representation using the inverse of the transformation in (A4):

$$\underline{s}_\omega(e)=\underline{\tilde{U}}^l(3\times3)\underline{s}_\omega(d)\,. \tag{A5}$$

We find in numerical studies on the Sr+Ar system that when the transformation (A5) is applied [using the numerically calculated $\underline{\tilde{U}}^l(3\times3)$ matrix] the $s_\omega(e)$ matrix elements from the full set of coupled equations (including all transition branches from a given initial J_0) agree with the $s_\omega(e)$ matrix elements calculated from the three separate sets of coupled equations which come from considering only one transition branch at a time, as in (30).

Any problems associated with asymptotic dressed-atom degeneracies can always be avoided by satisfying (A3) and calculating only one branch at a time. Our numerical calculations show that it is possible to calculate all branches simultaneously if the proper precautions are taken.

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