1. Introduction

Traditionally the study of spectral line shapes has concentrated on the measurement and interpretation of absorption or emission profiles. Often only the line widths were studied, however, especially in recent years, the quasi-static part of the spectrum has been used to obtain detailed information concerning intermolecular potentials (see, e.g., Ref. [1]). In this paper, we will evaluate the additional information that can be obtained by scattering light (usually from a laser) from an atomic system that is being perturbed by collisions. Such a scattering experiment is schematically illustrated in Figure 1. The scattering will be considered to be near resonant so that the laser frequency \( \omega_L \) is close to an atomic frequency \( \omega_o \). Several experiments of this type have been carried out in recent years [2-4]. The incident laser is characterized by frequency \( \omega_L \) and polarization \( \ell_1 \). The scattered light consists of two components, a (coherent) Rayleigh component \( \omega_R \) and a redistributed (fluorescent) component \( \omega_F \). The fluorescent component is characterized by its frequency \( \omega_F \) and polarization \( \ell_2 \).

Additional information is obviously included in this spectrum. For example, in order to obtain the absorption spectrum one merely asks the question:

What is the probability of absorbing a photon \( (\omega_L, \ell_1) \)?
Fig. 1. A scattering experiment.

Whereas, the specific state of the system just prior to the emission of a photon is obviously important for the fluorescence and its polarization, so that one must ask the question:

What is the probability of absorbing a photon \((\omega_L, \epsilon_1)\) and finishing up in a given Zeeman \((m^-)\) state which will give rise to \((\omega_F, \epsilon_2)\)?

The "AND" in this question is the key to the additional information since it indicates that, for scattering, the propagation between initial and final states is important (but, for absorption the final state of the system is irrelevant).

This physics can be illustrated in a particularly simple way by considering that the laser is detuned into the quasi-static wing of the atomic transition [5], as shown in Figure 2. The quasi-static absorption occurs at point \(R_0\) during a collision where the laser frequency matches the potential difference between the intermolecular potentials of the interacting atom–perturber pair (i.e. via the classical Franck-Condon principle). After this absorption the system flies apart (taking a time of order \(\tau_c\), the duration of collision) and subsequently fluoresces at a frequency \(\omega_F\) (close to \(\omega_0\)). The atom remains in the excited state for a time \(\tau_{-1}\).
Fig. 2. Scattering from quasi-static line wing.

where $\gamma_N$ is the natural decay rate, which is long compared with $\tau_C$ (and subsequent collisions may in fact take place during this time). Use of the quasi-static theory for absorption requires that the detuning $\Delta_L = \omega_L - \omega_0$ should obey $\Delta_L \tau_C \gg 1$ (so that the "time of interest" for absorption is "short"). Of particular relevance to this picture is the fact that the atomic states usually have degeneracy, and mixing between the various Zeeman substates occurs at large $R$. The polarization $\mathbf{e}_2$ of the fluorescence will, of course, depend critically on this mixing as the system flies apart.

Thus, by observing the fluorescence subsequent to absorption during a collision we are able to obtain information on the evolution of the system from the point of absorption to the completion of the collision. This contrasts with most atomic-collisions experiments where only scattering rates (through S-matrix elements for completed collisions) are obtained. This information on the intra-collisional evolution is the justification for the title of this paper, namely "Why half a collision is better than a whole one!"
Although this physical picture is very useful, we of course need a detailed theory for the scattering process. This picture does, however, show that we have to be very careful in our formulation, because the finite duration of the collision means that we should consider non-Markovian (non-impact) aspects and in addition initial correlations are important (since, in the line wings, absorption occurs during a collision, when the atom and perturber subsystem is highly correlated). This latter effect is usually ignored in line broadening calculations (by means of factorization of the initial density matrix), but is obviously of crucial importance in this case.

2. Mathematical Development

Basically two types of approach have been used to solve this problem in the binary collision regime. The first derives master equations for the density matrix and correlation functions in an atomic basis [5-8] whereas the second approach (and equivalent at weak laser fields) is formulated in terms of dressed (atom-radiation field) states [9-11].

In the first approach, the initial correlations are included ("destruction terms") and terms which represent both absorption and emission during collisions occur naturally in the formulation. Outside of the impact regime it is found that the scattered spectrum can no longer be characterized by simple absorption and emission profiles, but that the concept of profiles has to be generalized to take into account the final state after absorption (or initial state before emission). For example, the total fluorescence as a function of laser detuning may be written [7] as follows, in terms of summation over multipole index \( K \) and where, for convenience, collisional interaction of the lower state is neglected:

\[
I_F = I_L \sum K M_{23}^{(K)} \left[ \frac{2\tau^{(K)}(\Delta_L)}{\gamma_c^{(K)} + \gamma_N} - \frac{f(\Delta_L)}{\gamma_N^{(1)}(\Delta_L)} \right].
\]

(1)

Here \( \gamma_N \) is the natural width and \( \gamma_c^{(K)} \) is the relaxation rate (independent of \( \Delta_L \)) for the \( K \)th rank-excited state multipole (\( K = 0 \) “population,” \( K = 2 \)
"alignment" etc. [12]). $N_{23}^{(K)}$ contains dipole moment and polarization properties [13] and $I_L$ is the laser intensity.

Here $f(\Delta_L)$ is the usual "unified" absorption profile [14a,14b] obtained from

$$f(\Delta_L) = \frac{1}{\pi} \frac{\gamma^{(1)}(\Delta_L)}{(\omega_0 - \omega_L + \Delta^{(1)}_c(\Delta_L))^2 + \gamma^{(1)}(\Delta_L)^2}$$  \hspace{1cm} (2)

with $\gamma^{(1)}(\Delta_L) = \frac{1}{2} \gamma_N + \gamma^{(1)}_c(\Delta_L)$ where $\gamma^{(1)}_c(\Delta_L)$ and $\Delta^{(1)}_c(\Delta_L)$ are the "usual" frequency-dependent width and shift functions.

The generalized absorption profile $f_c^{(K)}(\Delta_L)$ (dependent on K) contains correlation effects due to absorption during a collision. For $\Delta_L$ large (compared to a line width $\gamma^{(1)}(\Delta_L)$), it may be written [5,7] as

$$f_c^{(K)}(\Delta_L) = \frac{1}{\pi} \frac{(\Gamma_c^{(K)}(\Delta_L) + \gamma_N/2)}{(\omega_0 - \omega_L)^2}.$$  \hspace{1cm} (3)

After performing an angle average over collision orientations, the generalised width $\Gamma_c^{(K)}(\Delta_L)$ can be expressed in terms of interaction-picture single-collision time-development operators $U_1(\tau,0)$ in the "collision frame." Here the binary collision approximation has been used [7,5], and $U_1(\tau,0)$ is calculated in terms of $V_1(\tau)$, the interaction between the radiating atom and a single perturber. Thus $\Gamma_c^{(K)}(\Delta_L)$ is given by

$$\Gamma_c^{(K)}(\Delta_L) = \text{Re} \sum_{p=N} \gamma_N (i\Delta_L - \gamma_N/2)^2 \int_0^\infty d\tau_1 e^{-\gamma N \tau_2} \int_0^\infty d\tau_1 e^{i(\Delta_L + i\gamma_N/2)\tau_1}$$

$$\times (-)^{\mu_5^{(j_e)} \mu_1^{(j_e K)}} \frac{j_e^{(j_e K)}}{\mu_4^{(j_e K)}} \frac{j_e^{(j_e K)}}{\mu_2^{(j_e K)}} \frac{j_e^{(j_e K)}}{\mu_1^{(j_e K)}}$$

$$\times [\langle j_e^{(j_e K)} \mid U_1(\tau_1,\tau_2) \mid j_e^{(j_e K)} \rangle | U_1(\tau_1,0) - 1 \rangle | j_e^{(j_e K)} \rangle_{Av} \rangle.$$  \hspace{1cm} (4)

The tilde ($\sim$) indicates tetradic operators. In the classical path picture $[\ldots]_{Av}$ represents the average over impact parameters and time of closest
approach, \( N_p \) is the perturber density and the sum (\( \mu's \)) is over the Zeeman (\( m' \)) states of the excited state (of angular momentum \( J_e \)).

Since the duration of the collision is in general short compared to \( \gamma^{-1} \)
the \( \tau_c \) integral can be easily performed, to give (leaving out matrix elements and vector coupling in order to illustrate the physics)

\[
\Gamma_c^{(K)}(\Delta_L) = -\text{Re} N_p \Delta_L^2 \sum_{\mu} \left[ \langle \langle \Omega_1^e(=0) | > > \int_0^\infty dt_1 e^{i \Delta_L \tau_1} \langle \langle \Omega_1^e(0,-\tau_1) - 1 | > > \right]_{AV}.
\] (5)

This clearly indicates the process of absorption (during time interval \( \tau_1 \)) and then the propagation, via \( \tilde{U}_1(=0) \), to specific states at the end of the collision. When \( \Delta_L \) is large compared to the inverse of the collision time \( \tau_c^{-1} \) there are essentially two contributions to the \( \tau_c \) integral in equation (5). The first occurs even in the absence of stationary phase points and leads (via steepest descents) (see [7]) to a contribution \( \gamma_c^{(K)}/2 \) to \( \Gamma_c^{(K)}(\Delta_L) \). Without this contribution, "negative" intensities would be obtained in the "antistatic" wing (where no quasi-static contribution occurs). The second contribution, the stationary phase part associated with \( U(0,-\tau_1) \), gives (when the stationary phase points are well separated) just the quasi-static absorption plus propagation to the completion of the collision discussed earlier. Thus

\[
\Gamma_c^{(K)}(\Delta_L) \sim \gamma_c^{(K)}/2 + \pi \text{Re} N_p \Delta_L^2 \sum_{\mu} \left[ \langle \langle \Omega_1^e(=0) | > > \langle \delta(\Delta_L - \Omega_1^e(0)) | > > \right]_{AV}
\]

\[
= \gamma_c^{(K)}/2 + \gamma_c^{(1)}(\Delta_L) \gamma_c^{(1)}(\Delta_L).
\] (6)

When \( \Delta_L \) is small compared to the inverse of the collision time \( \tau_c^{-1} \), it is straightforward to show that \( \Gamma_c^{(K)}(\Delta_L) \) reduces the impact limit result (i.e. \( \gamma_c^{(1)}(0) \) for no lower state interaction).

The \( \gamma_c^{(K)} \) factors in equation (1) take account of depolarization by subsequent collisions. The mathematics is complicated, but the physics is straightforward.
The alternative procedure, in terms of dressed states, relates the total fluorescent intensities to collision rates in the dressed frame (i.e. in this frame, in contrast to the atomic frame, the "impact" theory is valid [9]). Thus, it is only necessary to calculate dressed state S-matrix elements. It should also be noted that the dressed state calculations can handle arbitrary laser field intensities, whereas the previous results are limited to a low field expansion.

3. Calculations of the Polarization

Before proceeding further it is worthwhile looking at the experimental situation. Figure 3 shows the polarization data for Sr-Ar (defined by \( P = I_\parallel - I_\perp / I_\parallel + I_\perp \)) obtained by Alford [15]. These are for redistribution close to the strontium resonance line (460.7 nm) -- a \( j = 0 \) to \( j = 1 \) transition (\( ^1S + ^1P \)). Sr-Kr and Sr-Xe show much more dramatic dips [15] (down to \( \approx 20\% \) in the red wing).

We will henceforth concentrate on this example. For interaction with the spherically symmetric Ar atom, this gives rise to molecular states [16] with a \( ^1\Sigma \) ground state and \( ^1\Pi \) and \( ^1\Sigma \) excited states involving the coupling

![Polarization vs. \( \Delta_L (\text{cm}^{-1}) \)](image)

Fig. 3. Sr-Ar "zero pressure" polarization [15].
of three m-states \((0, \pm 1)\) (Fig. 4). Although seemingly simple these potentials are complicated by the \(\Pi-\Sigma\) curve crossing, which occurs at large internuclear separations (Fig. 4b).

![SrAr Potential Energy Curves](image)

Fig. 4. (a) Sr-Ar intermolecular potentials (after Julienne and Mies [16]). (b) Detail of excited state at large internuclear separation.
Our first attempt at calculating $P$ used simple attractive van der Waals potentials, i.e. $V(R) = C/R^6$ (with $C_\Sigma/C_{\Pi} = 7/4$, see [17]), which show no curve crossing (and $\Sigma$ always below the $\Pi$). The calculations, performed by C. V. Kunasz, were modeled after the four-state Light and Szöke calculations [17, see also 18]. The results for low laser intensities and in the zero pressure limit are shown in Figure 5. In this diagram, $\tau_C$ is defined in terms of the Weisskopf radius $R_C = (4C_\pi/3\psi)^{1/5}$ where $\psi$ is the mean interatomic velocity. In spite of the seeming simplicity of these calculations, when the detuning $\Delta_L$ is large, there are severe numerical problems. For large detuning, the number of oscillations associated with a detailed $S$-matrix calculation becomes very large and the structure of these $S$-matrix elements and transition probability (as a function of impact parameter) is quite complicated — see Figure 6 — (from Kleiber [19]). Beyond 40 cm$^{-1}$ the calculations become too time-consuming and expensive (in spite of using a CRAY-I).

Obviously, with all these oscillations, the stationary phase approach [as used to obtain eq. (6)] should be more tractable. During the collision an adiabatic (molecular state) representation of the collision is possible, thus, in terms of atomic states (for a collision frame with impact parameter

![Diagram](image)

Fig. 5. Polarization for van der Waals model (zero pressure: red wing: $C_{\Pi}/C_\Sigma = 4/7$).
Fig. 6. Transition probabilities between various dressed states as a function of impact parameter \( B \) (from [19]).

along the \( y_c \) direction [20]) we have the following non-vanishing matrix elements

\[
\langle 0 \mid U_1(t,0) \mid 0 \rangle = \frac{1}{2} \exp(-i \int_0^t V_0 dt)
\]

\[
\langle +1 \mid U_1(t,0) \mid +1 \rangle = \frac{1}{2} \exp[-i(\psi(t) - \phi(0))]
\times \left( \exp[-i \int_0^t V_0 dt] + \exp[-i \int_0^t V_2 dt] \right)
\]

\[
= \exp[-2i(\psi(t) - \phi(0))] \langle -1 \mid U_1(t,0) \mid -1 \rangle
\]

\[
\langle +1 \mid U_1(t,0) \mid -1 \rangle = \frac{1}{2} \exp[-i(\psi(t) + \phi(0))]
\times \left( \exp[-i \int_0^t V_0 dt] - \exp[-i \int_0^t V_2 dt] \right)
\]

\[
= \exp[-2i(\psi(t) + \phi(0))] \langle -1 \mid U_1(t,0) \mid +1 \rangle
\]
As shown in Figure 7, $\phi(t)$ is the angle between the position vector $\vec{R}(t)$ and the $y_c$ axis. These matrix elements (labeled by $|m\rangle$) indicate how absorption to either the $\Sigma$ or $\Pi$ state can occur at the stationary phase points (i.e. where $\Delta\omega = v_{\Pi}(0) = c_{\Pi}/R_{\Pi}^6$ and $\Delta\omega = v_{\Sigma}(0) = c_{\Sigma}/R_{\Sigma}^6$). At large internuclear separations, the molecular states decouple and these adiabatic states are no longer valid. A simple procedure is to assume that those molecular states are valid until they decouple to a superposition of atomic states at roughly the Weisskopf radius $R_C$ (which is the radius at which the rate of rotation $\phi$ of the molecular axes cannot be ignored [21]). Such an approach has been used in the line broadening context by (e.g.) Lewis et al. [23a,23b] and Masnou-Seeuws and Roueff [22]. This geometry is indicated for a straight line trajectory in Figure 7. With this approximation it is straightforward [after evaluating the vector coupling in eq. (4)] to obtain the quantities $a^{(K)}$, defined in equation (6).

Specifically, $a^{(0)} = 1$ and

$$a^{(2)}(\Delta_L) = \frac{1}{6} + \frac{1}{10} [2<\cos(\phi_c - \phi]\rangle + <\cos 2(\phi_c - \phi]\rangle] + \frac{1}{10} g(\Delta_L) [\frac{1}{30} + \frac{1}{10} <\cos 2(\phi_c - \phi]\rangle]$$

$$\frac{2}{3} + \frac{1}{3} g(\Delta_L)$$

(8)

![Fig. 7. Collision geometry for a straight line trajectory.](image-url)
where \( g(\Delta_L) \) is the ratio between the \( \Sigma \) and \( \Pi \) quasi-static absorption profiles at frequency \( \Delta_L \), e.g., for our van der Waals model \( g(\Delta_L) = (C_\Sigma/C_\Pi)^{1/2} \).

Here \( \langle ... \rangle \) represents \( \int_{-\pi/2}^{\pi/2} \ldots \cos \phi d\phi \) which comes from the average over all times of closest approach. From these results

\[
P = \frac{3a^{(2)}(\Delta_L)}{2 + a^{(2)}(\Delta_L) + \frac{2\gamma_c^{(2)}}{\gamma_N}}.
\]  

(9)

The \( \gamma_c^{(2)} \) term represents depolarization due to subsequent collisions.

The zero pressure result for this model with straight line trajectories is shown in Figure 5. To obtain these results we had to ignore some cross terms in the tetradic product \( \tilde{U}(\omega,0) \), like

\[
\exp(-i \int_0^\infty (V_\Sigma - V_\Pi) dt) \equiv e^{-i\eta}
\]

which occur [from eq. (7)] due to interference between the amplitudes associated with propagation along \( \Pi \) and \( \Sigma \) curves after absorption. This effect is similar to the familiar interference between stationary phase points [24], however, on leaving the region of large potential \( V(R) \) (on the way out from the collision) the phase shift \( \eta \) can be quite small (whereas \( \eta \) is quite large, and hence there are rapid oscillations, for trajectories for which absorption occurs on the way in and which go through a region where \( V(R) \) is large; see Fig. 7). A simple estimate gives \( \eta = 0.2(\Delta_L T_c)^{5/6} \). We obtain \( \eta \sim 2\pi \) for which \( \langle e^{-i\eta} \rangle \sim 0 \) when \( \Delta_L \sim 300 \text{ cm}^{-1} \), which explains the merging with the asymptotic results in this region. We note that uncertainty in the actual point of stationary phase can change \( \eta \) by \( -1 \). Thus, \( \Pi \) and \( \Sigma \) absorptions are independent only beyond \( \sim 300 \text{ cm}^{-1} \) for the \( C_\Sigma/C_\Pi = 7/4 \) case.

These interference effects are quite subtle. The use of a \( \delta \)-function in equation (6) actually is incorrect for interferences, i.e., when stationary phase points are not well separated (since there are stationary phase points in both the \( \tau_1 \) integral and the time of closest approach, \( t_0 \), integral implied in equation (5) — see refs. [24] and [28]). A more careful
analysis, following [24] and [28], shows that $e^{-i\eta}$ terms still occur but now $\eta$ actually corresponds to the phase difference for propagation to the completion of the collision from actual $\Sigma$ and $\Pi$ points of stationary phase. However, the above estimate for $\eta$ still remains valid for the case under consideration. If absorption to e.g. $\Pi$ only occurred (see below) we note that these $\Pi/\Sigma$ interferences would be absent.

Detailed numerical calculations (performed by S. V. O'Neil), which integrate the equations for the time development operator (see ref. [20]) through the region of mixing of states, confirm the validity of this cutoff model (and the estimate for $\eta$) and lead to results within ~1% of those obtained with this simple model. [Grosser [27] has recently reached similar conclusions relative to the validity of this model in a study of atom-atom scattering.]

The adiabatic limit for this model (corresponding to $R_\infty \rightarrow \infty$), when molecular states can be used throughout, is $P = 17\%$. Our results converge very slowly onto this value since the polarization varies via the slowly varying quantity $1/(\Delta_{\Sigma}^+ C_\Sigma)$. Changing the $C_\Sigma/C_\Pi$ ratio has little significance -- for example, $C_\Sigma/C_\Pi = 4$ (as used by ref. [20]) reduces $P$ by at most 2% in the 100-1000 cm$^{-1}$ region and changes the asymptotic value to 14%. We note that the results in Figure 5 are in qualitative agreement with those of Ref. [5].

As indicated earlier (in Fig. 4) this van der Waals approximation, although convenient for calculation (and probably not completely unrealistic for the impact limit) is not useful for large detunings since the $\Sigma$ state becomes repulsive. Thus, absorption should occur to the $\Pi$ state only and polarizations can immediately be obtained from equation (8) with $g(\Delta_\Sigma) = 0$ (i.e. no $\Sigma$ absorption). These results, for a van der Waals potential for the $\Pi$ state only, are shown in Figure 8. When a minor error in Lewis et al. [23b] is corrected, their results are in agreement with those presented here. The asymptotic polarization is $P = 3/11$. In contrast, an asymptotic polarization of zero would be obtained if absorption occurred to the $\Sigma$ state only.
Fig. 8. Polarization for absorption to \( \Pi \) state (red wing: \( g(\Delta L) = 0 \)).

The results from equation (8) actually only depend on \( x = R_{0\Pi}/R_c \)
(\( \approx 1.18(1/\Delta L R_c)^{1/6} \) for the assumed van der Waals \( \Pi \) potential) and again show slow convergence to asymptotic limit. However, the polarization decreases monotonically as \( R_{0\Pi}/R_c \) decreases (irrespective of assumed potential). Yet, Figure 3, the experimental polarization increases in the far wing. Equation (8) gives a clue to what is going on, since when absorption occurs to the \( \Pi \) state only, the quantity \( q^{(2)}(\Delta L) \) (and hence the zero pressure \( P \)) depends only on the angle of rotation of the molecular dipole which is created by the laser absorption, i.e. only on \( (\phi_c - \phi_\Pi) \).

Figure 9 illustrates a simple model for which a hard sphere of radius \( R_s \ll R_{0\Pi} \) causes the rotation of the molecular dipole to be restricted to the angle \( \theta \). This model gives an asymptotic polarization of 45% (\( = 21/47 \)) (using \( V_{\Pi} = C_c/R_c^6 \) outside of the hard sphere), and shows the trend of decreasing polarization with increasing detuning. For no rotation of the molecular axis \( P = 7/9 = 78\% \) (obtained from \( x = 1 \)), a result which has recently been obtained by Vigué et al. [25] during a study of photodissociation of \( \text{Ca}_2 \) molecules.
Fig. 9. Collision geometry for a hard sphere collision.

Use of a "sudden approximation" in which there is no coupling to form molecular states [26] gives a polarization $P$ of $50\%$.

4. Conclusions

These simple models show that the polarization $P$ of the fluorescence is quite strongly dependent on the mixing of the Zeeman-states at large $R$ (via $x = R_0/R_c$ of our model) and also on the amount of rotation of the molecular dipole formed during the collision. In addition, interference between possible routes of absorption may occur. Thus, the interpretation of the polarization requires detailed knowledge of the evolution of the system from the point of absorption. In addition, when the ground state is isotropic (i.e. $K = 0$, as with the $^1\Sigma$) the total intensity $I_T/I_L = (I_{u} + 2I_{l})/I_L$ is directly proportional to $f(\Delta_L)$ so that the usual analysis of the quasi-static profiles [1] will yield the intermolecular potentials. Further, the use of equation (9) as a function of density at any convenient detuning [15] yields the destruction of alignment rate $\gamma_c^{(2)}$. 
This wealth of information, coupled with the fact that these scattering experiments are reasonably straightforward to perform, makes light scattering a very useful tool for the evaluation of intra-collisional interactions.

Acknowledgments

The author wishes to acknowledge help, stimulation and encouragement from his colleagues — K. Burnett, R. Ballagh, A. Ben-Reuven, C. V. Kunasz, S. V. O'Neil, W. J. Alford, P. Kleiber, A. Szőke and A. Gallagher. Support for this work was through the National Science Foundation, the National Aeronautics and Space Administration (grant NGL-06-003-057), the Atomic and Plasma Radiation Division of NBS, and a computing grant from the National Center for Atmospheric Research (administered by NSF and NCAR).

References

15. W. J. Alford, K. Burnett and J. Cooper: These proceedings.