Spectroscopic Detection Methods
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9.1 Theoretical Background and Methodology
Spectroscopic detection of atomic and molecular species in molecular beam scattering involves nearly exclusively lasers. State selective detection of molecules with closely spaced levels requires both narrow spectral band width and high spectral intensity. Except for the region very close to the nozzle and a few atomic species such as sodium, the density of particles is too small for conventional spectroscopic techniques to be useful for detection purposes.

The basic properties of absorption and emission of light are discussed in this chapter. Emphasis is on the detection of atoms and diatomic molecules interacting with polarized laser light. Most of the results are applicable to triatomic or polyatomic molecules, provided the appropriate line strength factors are known. In polyatomic molecules, however, the population is spread over a larger number of quantum states than in diatomics. The laser-induced fluorescent intensity from an individual quantum state will therefore be rather small. Nevertheless, the combination of state-of-the-art molecular beam techniques with laser-based detection methods will allow state-selective scattering experiments with polyatomic species, at least in favorable cases (see, e.g., van Hulst, ter Meulen, and Dymanus, 1986, 1987).

Preparation and detection of oriented molecules has been reported recently for a few species. We are only in the beginning stage of understanding of the role of alignment in inelastic and reactive scattering in collisions with molecules or surfaces; this will be an area of active research in the near future. The problems related to detecting and preparing aligned species are therefore discussed in detail here and in Chapter 12, respectively.

Spectroscopic detection techniques have been the subject of previous review articles. For example, Kinsey (1977a) discusses the technique of laser-induced fluorescence, and Levy (1980) summarizes some aspects pertinent to the spectroscopy of cold molecules in beams. A detailed quantitative analysis, in particular related to molecular polarization, is presented by Case, McClelland, and Herschbach (1978) as well as by Greene and Zare (1983), while Altkorn and Zare (1984) considered the effect of saturation. Photoionization is a more recent detection technique that has also been discussed previously, for example, by Hurst, Payne, Kramer, and Young (1979) and by Johnson and Otis (1981). A quantitative analysis of resonantly enhanced
two-photon ionization has been given very recently by Jacobs and Zare (1986) as well as Jacobs, Madix, and Zare (1986). An excellent introduction into laser spectroscopy in general is given by Demtröder (1981). Some details relevant to molecular beam experiments, concerning spectroscopic features and sensitivity of detection, are also discussed in Volume 2, Chapter 7. Some recent applications to collision dynamics problems are summarized in the book by Jackson and Harvey (1985). In this chapter, emphasis is on the relationship between observed signals and molecular properties, methodology, and experimental hardware for spectroscopic detection in the visible and near ultraviolet. Only representative articles have been chosen as references; a more complete coverage of the related literature can be found in Chapters 12, 23, and 24. Infrared spectroscopy has been very successful in beam experiments, in combination with bolometric detection. This latter technique is discussed in detail in Chapter 6 of Volume 2.

9.1.1 Absorption and Emission of Light

9.1.1.1 Introduction. The detection probability, $D(i)$, of a molecule in the quantum state, $i$, will be derived in the following. In most cases of interest, the index "$i$" represents the vibrational, rotational, and orientational quantum numbers $v$, $j$, and $m$, respectively, but other quantum numbers may be included as well. It is assumed that the laser frequency $\nu(i,f)$ is tuned to an $i \rightarrow f$ transition. The labels $i$ and $f$ are used for levels in different electronic states. $D(i)$ factorizes as

$$D(i) = \sum_f E(i,f)K(f)$$  \hspace{1cm} (9.1)

where $E(i,f)$ is the excitation probability and $K(f)$ gives the probability of detecting a photon from molecules in the excited state, $f$.

In the limit of small excitation probability, the familiar expression

$$E(i,f) = W(i,f)\Delta t_i \quad \text{for } E(i,f) \ll 1$$  \hspace{1cm} (9.2)

applies, where $W(i,f)$ is the induced optical transition rate that depends on molecular properties such as the electronic transition probability, the Franck–Condon factors $F_{ij}$, the rotational line strength factors $S_{ij}$, and the spectral energy density $\rho(\omega)$ of the laser. The interaction time, $\Delta t_i$, of the molecules with the laser is determined either by the length, $\Delta t_{l_i}$, of the laser pulse or by the laser beam diameter, $d$, and velocity, $v$, of the molecule, $\Delta t_i = d/v$. If $E(i,f) \ll 1$ is not valid, equation (9.2) does not apply, and the excitation probability must be determined by solving the appropriate rate equations (see section 9.1.2). The detection probability of a photon

$$K(f) = \sum_l \eta_l C(f,l)T(\nu_l)Q(\nu_l)$$  \hspace{1cm} (9.3)

includes all the relevant quantities for the emission process and for the transfer of the photons to the detector. The sum is over all levels $l$, accessible from level $f$. The quantum yield, $\eta_l$, for the emission of a photon of frequency $\nu_l$, will deviate from unity only if nonradiative processes compete with the radiative decay. Collisional quenching, like collision-induced dissociation of the
excited state, is considered to be negligible in molecular beam environments. It is also assumed that the electronic lifetime, τ, is short compared with the residence time in the sensitive area of the detector. Otherwise, corrections must be applied (see section 9.1.3.1).

The collection probability, \( C(f, l) \), for the photons is given by

\[
C(f, l) = \int P_m(f, l, \mathbf{k}_r) G(\mathbf{k}_r) \, d\Omega_r, \tag{9.4}
\]

The term \( P_m \) characterizes the spatial distribution of photons emitted from level \( f \) with \( \mathbf{k}_r \) being the direction of photon emission. It also includes the Franck-Condon factor for the \( f \rightarrow l \) transition. \( G(\mathbf{k}_r) \) is the angle-dependent collection efficiency of the optics. The ideal detector would be characterized by \( G(\mathbf{k}_r) = 1 \) for all values of \( \mathbf{k}_r \). Typically, however, \( G(\mathbf{k}_r) = 1 \) is valid only within a cone of solid angle \( \Delta \Omega \) and \( G = 0 \) elsewhere. \( P_m \) depends on the orientation of the molecule in space and on the type of the \( f \rightarrow l \) transition [see equation (9.52)]. It is isotropic only for an ensemble of molecules with isotropic distribution of angular momenta in the excited state, \( f \). Uniform \( m \)-level population is rarely ensured in molecular beam experiments, however, and a careful analysis of the variation of \( C(f, l) \) with the orientational quantum number \( m \) is required. Under favorable conditions one can make use of magic angles between the laser polarization, \( \hat{e} \), and the axis of symmetry of the collection optics to eliminate the \( m \)-level dependence of the quantity \( C(f, l) \) (see sections 9.1.1.8 and 9.1.5).

Finally, \( T(\nu_n) \) of equation (9.3) is the spectral transmission function for photons to the detector, determined by the spectral properties of the collection optics (coated lenses or mirrors and filters) and, for example, the fiber optic transmission lines. The quantum efficiency of the detector is \( Q(\nu_n) \). If the fluorescent emission covers only a narrow spectral range, the variation of \( T \) and \( Q \) with \( \nu_n \) may be small, and these quantities can be treated as constants.

The various factors included in equation (9.1) depend on the given experimental conditions. It matters, for example, whether continuous-wave (CW) or pulsed lasers with high or low power and small or broad spectral bandwidth are used. Their relationship to the basic molecular properties is discussed in more detail next.

9.1.1.2 Optical Transition Rates. The interaction of radiation with atoms and molecules is discussed in many textbooks (see, e.g., Steinfield 1974, Yariv 1975, Allen and Eberly 1975, Letokhov and Chebotayev 1977; Demtröder 1981; Fontana 1982). Only a brief comprehensive discussion of the most relevant basic formulas is given here.

Consider a monochromatic plane wave of frequency \( \omega \), wave vector \( \mathbf{k} \), polarization \( \hat{e} \), and vector potential \( \mathbf{A} \)

\[
\mathbf{A}(\omega) = \frac{1}{2} A_0(\omega) \hat{e} [e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}] \tag{9.5}
\]

The relation of \( \mathbf{A} \) and the electric field vector \( \mathbf{E} \) is given by Maxwell’s equation (see, e.g., Jackson 1962)

\[
\mathbf{E} = \frac{1}{c} \frac{\partial}{\partial t} (\mathbf{A})
\]
leading to

\[ A_{0}(\omega) = i \frac{c}{\omega} E_{0}(\omega) \]  

(9.6)

for the corresponding amplitudes. The Hamiltonian of the molecule with wave function \( \psi_{i} \) and total energy \( E_{i} \) interacting with the field is \( H = H_{0} - (e/mc)pA \), where \( H_{0}\psi_{i} = E_{i}\psi_{i} \). First-order time-dependent perturbation theory yields the transition amplitude \( c_{\sigma}(t) \) from state \( i \) to state \( f \). With \( c_{i}(0) = 1 \) and \( c_{f}(0) = 0 \), the result is (see e.g., Merzbacher 1970; Messiah 1974)

\[ c_{\sigma}(t) = -\frac{i}{\hbar} \int_{0}^{t} dt' e^{i(E_{f} - E_{i})t'} \left( \psi_{f} \right| \frac{-e}{mc} pA \left| \psi_{i} \right) \]  

(9.7)

The extension of molecular orbitals is small compared with the wavelength of the optical field. Thus, applying the dipole approximation \( (kr \ll 1) \) in equation (9.7) yields, with equations, (9.5) and (9.6),

\[ c_{\sigma}(t) = \frac{e}{\hbar m \omega} \frac{E_{0}(\omega)}{2} \left( \psi_{f} \right| p\hat{e} \left| \psi_{i} \right) \int_{0}^{t} dt' e^{i\omega_{0}(t' + \tau)} \left( e^{-i\omega_{0} \tau} + e^{i\omega_{0} \tau} \right) \]  

(9.8)

where \( \hbar \omega_{0} = E_{f} - E_{i} \). The validity of the dipole approximation may be questionable for Rydberg states with large principal quantum numbers (Leuchs, Smith, Dixit, and Lambropoulos 1986). Since \( e^{i\omega_{0}(t' + \tau)} \) is a rapidly oscillating function, the corresponding part of the integral cancels (Allen and Eberly 1975; Letokhov and Chebotayev 1977), while \( e^{i\omega_{0}(t' - \tau)} \) approaches unity for near-resonance excitation \( (\omega \rightarrow \omega_{0}) \). Thus, equation (9.8) reduces to

\[ c_{\sigma}(t) = \frac{e}{\hbar m \omega} \frac{E_{0}(\omega)}{2} \left( \psi_{f} \right| p\hat{e} \left| \psi_{i} \right) \int_{0}^{t} dt' e^{i(\omega_{0} - \omega)\tau} \]  

(9.9)

With the help of

\[ [H_{0}, \hat{r}] = \frac{\hbar}{im} \hat{p} \]

the matrix element in equation (9.8) is transformed from impulse to length form (Messiah 1974)

\[ \left( \psi_{f} \right| \hat{p} \hat{r} \left| \psi_{i} \right) \]  

(9.10)

Evaluation of the integral of equation (9.9) yields

\[ J(t) = \int_{0}^{t} dt' e^{i(\omega_{0} - \omega)\tau} = \frac{1}{i(\omega_{0} - \omega)} \left( e^{i(\omega_{0} - \omega)\tau} - 1 \right) \]

which can be rewritten, to give

\[ J(t) = 2 \frac{\sin(\omega_{0} - \omega)\tau}{i(\omega_{0} - \omega)} \frac{\tau^{2}}{2} e^{i(\omega_{0} - \omega)\tau^{2}} \]  

(9.11)

The transition rate per unit time is

\[ W_{\sigma} = \int \lim_{t \to \infty} \frac{|c_{\sigma}(t)|^{2}}{t} d\omega \]  

(9.12)

Since (Messiah 1974)

\[ \lim_{t \to \infty} \frac{|J(t)|^{2}}{t} = 2\pi \delta(\omega_{0} - \omega) \]  

(9.13)
the transition rate vanishes for \( \omega_f \neq \omega \), because a finite lifetime of the level \( f \) has not yet been introduced. The result is

\[
W_\gamma = \frac{\pi e^2}{\hbar^2 \epsilon_0} \rho(\omega_f) |\langle \psi_f | \hat{r} \hat{F} | \psi_f \rangle|^2
\]  

(9.14)

where

\[
\rho(\omega_f) = \frac{1}{2} \epsilon_0 E_0^2(\omega_f)
\]  

(9.15)

has been used to replace the field amplitude by the spectral energy density \( \rho(\omega_f) \). Introducing the transition dipole moment, \( \mu_f = e \langle \psi_f | \hat{r} | \psi_f \rangle \), the transition rate reads

\[
W_\gamma = \frac{\pi}{\hbar^2 \epsilon_0} (\hat{F}_f \mu_f)^2 \rho(\omega_f)
\]  

(9.16)

The relation of \( \mu_f \) and the electronic lifetime, \( \tau \), is given in equation (9.65).

9.1.1.3 Line Shape Problems. Equation (9.16) implies that spontaneous decay of level \( f \) does not occur. Although line-shape-related problems are discussed in more detail in Chapter 7 of Volume 2, a few comments are in order here. Including spontaneous decay, equation (9.12) reads (Messiah 1974; Demtröder 1981)

\[
W_\gamma(\omega) = \int \lim_{t \to \infty} \frac{|c_f(t, \omega)|^2}{t} e^{-\gamma t} d\omega
\]  

(9.17)

and equation (9.13) must be replaced by

\[
\lim_{t \to \infty} \frac{|F(t, \omega)|^2}{t} e^{-\gamma t} = \frac{\gamma}{2} \frac{1}{(\omega_f - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}
\]  

(9.18)

It is convenient to introduce

\[
g(\omega) = \frac{1}{\pi \gamma} L(\omega)
\]  

(9.19)

with the Lorentzian line shape function

\[
L(\omega) = \frac{\gamma^2}{(\omega_f - \omega)^2 + \left(\frac{\gamma}{2}\right)^2}
\]  

(9.20)

where \( \gamma \) is the full width at half maximum (FWHM) of the profile. These functions are normalized such that

\[
\int g(\omega) \, d\omega = 1
\]  

(9.21)

and

\[
L(\omega_f) = 1
\]  

(9.22)

Equation (9.16) then reads

\[
W_\gamma = \frac{\pi}{\hbar^2 \epsilon_0} (\hat{F}_f \mu_f)^2 \cdot \int \rho(\omega) g(\omega) \, d\omega
\]  

(9.23)

with \( (\hat{F}_f \mu_f)^2 = e |\langle \psi_f | \hat{r} \hat{F} | \psi_f \rangle|^2 \). The rate \( W_\gamma \), with \( (\hat{F}_f \mu_f)^2 \) expressed
in more readily accessible molecular properties such as electronic lifetimes and Franck-Condon factors, is given in equation (9.66). Equation (9.23) is inspected in some further detail because inappropriate approximations to the integral are a common source of errors that easily escape unidentifiable but may cause disagreement between calculated and observed data.

The intensity, I, or energy density, ρ₀, of a laser source is more readily available than the distribution of spectral energy density

$$\rho(\omega) = \rho_0 f(\omega)$$  \hspace{1cm} (9.24)

I and ρ(ω) are related by

$$I = c \int \rho(\omega) \, d\omega$$  \hspace{1cm} (9.25)

The distribution function, f(ω), is normalized according to

$$\int f(\omega) \, d\omega = 1$$  \hspace{1cm} (9.26)

This leads, with equations (9.19) through (9.25), to

$$W_f = \frac{(\epsilon n_0)^2}{\hbar^2 \epsilon_0} \frac{2}{c \gamma} F$$  \hspace{1cm} (9.27)

where

$$F = \int f(\omega)L(\omega) \, d\omega$$  \hspace{1cm} (9.28)

depends on the mutual overlap of shape of the spectral energy density distribution functions, f(ω), and the line shape function, L(ω).

Using CW lasers implies, in most cases, a spectral bandwidth of the light source γ_L that is small compared with the width γ of the absorption profile (γ_L ≪ γ; see Fig. 9.1a). This leads to

$$F = L(\omega_L)$$  \hspace{1cm} (9.29)

which reduces, for excitation on resonance (ω_L = ω_0), to

$$F = 1$$  \hspace{1cm} (9.30)

For pulsed lasers, γ_L ≫ γ (Fig. 9.1b) holds and

$$F = f(\omega_0) \frac{\gamma}{2 \pi}$$  \hspace{1cm} (9.31)

results. For a Fourier-limited pulse, a Lorentzian form of f(ω) is expected and f(ω_0) = (2/π) \cdot (1/γ_L) is valid, provided the maximum of ρ(ω) is at ω_0, leading to

$$F = \frac{\gamma}{\gamma_L}$$  \hspace{1cm} (9.32)

Only special cases have been discussed. Obviously, an accurate calculation of the rate of laser-induced transitions by equation (9.23) requires an accurate determination of the relevant spectral energy density distribution. Unfortunately, this is rarely easy to do for pulsed or multimode CW lasers.

9.1.1.4 General Aspects of Polarization Characteristics. The intensity and spatial distribution of laser-induced fluorescence is obtained by inserting W_f from equation (9.27) into the appropriate
rate equations (see section 9.1.2). Before we do so, we will inspect the properties of the transition dipole matrix element in further detail, with its geometric part, \( \mathbf{r} \cdot \hat{e} \), as well as the molecular properties, introduced by integrating over the appropriate wave function. This is important because, for detection purposes, nearly exclusively polarized laser radiation is used, resulting in non-isotropic emission of fluorescence radiation.

Consider a plane wave with wave vector \( \mathbf{k} \) in the space-fixed coordinate system \((x, y, z)\) (Fig. 9.2). The polarization vector \( \hat{e} \) is in the plane spanned by \( \hat{u}_1 \) and \( \hat{u}_2 \). For circularly polarized waves, it is given by (Fontana 1982)

\[
\hat{e}^\pm = \pm \frac{1}{\sqrt{2}} (\hat{u}_1 \mp i \hat{u}_2)
\]  
(9.33)

The upper and lower signs apply to right-hand and left-hand polarization, respectively. Transformation to linear polarization is achieved by

\[
\hat{u}_1 = \frac{1}{\sqrt{2}} (\hat{e}^+ - \hat{e}^-), \quad \hat{u}_2 = \frac{i}{\sqrt{2}} (\hat{e}^+ + \hat{e}^-)
\]  
(9.34)

The dipole operator for circularly polarized light reads, with the electronic coordinate \( \mathbf{r} = \mathbf{r} \cdot \hat{e} \),

\[
r \cdot \hat{e}^\pm = \left(\frac{4\pi}{3}\right)^{1/2} r Y_{1,\pm 1}(\hat{e})
\]  
(9.35)

Expression of \( \mathbf{r} \cdot \hat{e} \) in the space-fixed coordinate system \((x, y, z)\) is achieved by rotating the coordinate system \( \hat{u}_1, \hat{u}_2, \mathbf{k} \) through \(-\theta_x, -\phi_x\) to align \( \mathbf{k} \) with the quantization axis, \( \hat{z} \), as well as \( \hat{u}_1 \) and \( \hat{u}_2 \) with \( \hat{x} \) and \( \hat{y} \), respectively. This leads to

\[
Y_{1,\pm 1}(\hat{e}) = \sum_{\Delta m} D_{\Delta m, 0}^{1, \pm 1}(-\phi_x, -\theta_x, 0) Y_{1,\Delta m}(\hat{e})
\]  
(9.36)

with \( \Delta m = 0, \pm 1 \). In the space-fixed coordinate system, the dipole operator for circularly polarized light reads

\[
r \hat{u}_i = \frac{1}{\sqrt{2}} (r \hat{e}^+ - r \hat{e}^-) = \frac{r}{\sqrt{2}} \left(\frac{4\pi}{3}\right)^{1/2} \sum_{\Delta m} D_{\Delta m,-1}^{1,1}(-\phi_x, -\theta_x, 0) Y_{1,\Delta m}(\hat{e})
\]  
(9.37)

which reduces again to equation (9.35) if \( \hat{k} \) is along the \( z \)-axis. For linear polarization parallel to the \( x \)-axis and propagation along the \( z \)-axis, equations (9.34) and (9.37) lead to

\[
r \hat{u}_i = \frac{1}{\sqrt{2}} (r \hat{e}^+ - r \hat{e}^-) = \frac{r}{\sqrt{2}} \left(\frac{4\pi}{3}\right)^{1/2} \sum_{\Delta m} \left[ D_{\Delta m, -1}^{1,1}(0, -\pi/2, 0) - D_{\Delta m, -1}^{1,1}(0, \pi/2, 0) \right] Y_{1,\Delta m}(\hat{e})
\]  
(9.38)

which reduces to

\[
r \hat{u}_i = \left(\frac{4\pi}{3}\right)^{1/2} r Y_{1,0}(\hat{e})
\]  
(9.39)

because \( D_{\pm 1,0}^{1,1}(0, -\pi/2, 0) = 1/2 \) is valid for all combinations of plus and minus signs and \( D_{0,\pm 1}^{1,1} = \mp 1/\sqrt{2} \). The dipole operators for other polarization states are given in Table 9.1 (see, e.g., Fontana 1982).

If the application of the Born–Oppenheimer approximation is justified for the electronic states involved, the wave functions
factorize in an electronic, vibrational, and rotational part (Herzberg 1950)

$$\psi = \psi^e(r, R)\psi^v(R)\psi^R(\hat{\mathbf{k}})$$  \hspace{1cm} (9.40)

where $R$ is the internuclear separation. The wave functions $\psi^e$ and $\psi^v$ are affected by $|r|$ and $\hat{r} \cdot \hat{e}$ of the dipole operator, respectively. The matrix element of equations (9.14) and (9.27) then reads

$$|\langle \psi_f | \hat{e} \cdot \hat{e} | \psi_i \rangle|^2 = |\langle \psi_f | \hat{r} | \psi_i \rangle|^2 |\langle \psi_f | \psi_i \rangle|^2 |\langle \psi_f | \hat{e} \cdot \hat{e} | \psi_i \rangle|^2$$  \hspace{1cm} (9.41)

The first term on the right-hand side is proportional to the square of the electronic transition dipole, the second is the Franck-Condon factor, and the third contains all information on polarization phenomena. It includes the line strength factors. Equation (9.41) is usually evaluated in a molecule-fixed coordinate system. Transformation of the dipole operator from the space-fixed system into the molecular system yields, after using the Wigner–Eckart theorem (Edmonds 1957),

$$|\langle \psi_f | \hat{e} \cdot \hat{e} | \psi_i \rangle|^2 = \frac{4\pi}{3} \cdot D_2(\hat{e}) \left( \begin{array}{c} j_i \ \ 0 \ \ j_f \end{array} \right) \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & m_i & m_r \\ 0 & 0 & m_r \end{array} \right) \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & m_i & m_r \\ 0 & 0 & m_r \end{array} \right) \left( \begin{array}{c} 0 \\ 0 \\ 1 \end{array} \right)$$

$$\times |\langle a_{j_i} | D_2 | a_{j_f} \rangle|^2$$  \hspace{1cm} (9.42)

The total angular momenta and their projection on a space-fixed axis in the initial and final states are $j_i, j_f$, and $m_i, m_r$, whereas $a_{\alpha m}$ combines all other quantum numbers defined in the molecular-fixed frame. The factor written as a 3j-symbol is zero except for $\Delta m = m_f - m_i = 0, \pm 1$.

$D_2(\hat{e})$ is a linear combination of rotation matrix elements depending on the laser polarization, $\hat{e}$, and direction of incidence, $\hat{\mathbf{k}}$. For circular polarization with $\hat{\mathbf{k}}$ parallel to $\hat{e}$

$$D_2(\hat{e}) = |D_{\alpha m, \pm 1}(\hat{k})|^2$$  \hspace{1cm} (9.43a)

is valid, whereas for linear polarization parallel to $\hat{e}$ or $\hat{f}$,

$$D_2(\hat{e}) = \frac{1}{2} |D_{\alpha m, +1}(\hat{k}) - D_{\alpha m, -1}(\hat{k})|^2$$  \hspace{1cm} (9.43b)

results. The functions $D_{\alpha m, \pm 1}(\hat{k})$ are given in equation (9.53). If $\hat{\mathbf{k}}$ is parallel to $\hat{e}$ and the linear polarization is parallel to $\hat{f}$, the angular
factor is given by

\[ D_4(\theta) = \frac{1}{2} \delta_{a_m,b} \]  

(9.43c)

9.1.1.5 Line Strength Factors The last factor on the right-hand side of equation (9.42) is the square of the reduced matrix element, and is independent of the projection quantum numbers, \( m_i \), in the space-fixed coordinate system but depends on the molecular wave functions. It is convenient to introduce a line-strength factor (Kovacs 1969)

\[ S_{ji} = \frac{4\pi}{3} |\langle a_j| D_i || a_j \rangle|^2 \]  

(9.44)

The angular part of the wave functions, \( |a_j \rangle \), depends on the actual coupling scheme of angular momenta in the molecule such as the angular momentum \( N \) of the nuclei, the component \( \Omega \) of the electronic angular momentum on a molecular axis, as well as the electronic spin, \( S \), and possibly the nuclear spin, \( I \). Evaluation of equation (9.44) yields the \( j \) and \( \Omega \)-related selection rules for optical transition.

In general, calculation of the line-strength factors requires complex angular momentum algebra. The \( S_{ji} \) values are easily available for coupling according to pure Hund's coupling cases, most notably cases a and b (Herzberg 1950) (Fig. 9.3).

Hund's case a (Fig. 9.3a) applies to symmetric tops (molecules with one axis of symmetry) with the electronic angular momentum \( L \) and spin \( S \) (if any) coupled to the axis to give \( \Lambda \) and \( \Sigma \), respectively. The latter two add up to \( \Omega = \Lambda + \Sigma \). The line-strength factor is then given by (Kovacs 1969)

\[ S_{ji} = \gamma |j_i \rangle \frac{1}{\Delta \Omega \Omega_j} (2j_i + 1)(2j_i + 1) \]  

(9.45)

with \( \gamma = 1 \) for \( \Delta \Omega = 0 \) and \( \gamma = 1/4 \) for \( \Delta \Omega = \pm 1 \). Examples of the former case are \( \Sigma \leftrightarrow \Sigma \) and \( \Pi \leftrightarrow \Pi \) transitions with arbitrary multiplicities, \( s \), while the latter applies to \( \Sigma \leftrightarrow \Pi \) transitions, for example. For Hund's case b (see Fig. 9.3b) the result is

\[ S_{ji} = \gamma \langle k_i | j_i \rangle \frac{1}{\Lambda \Lambda_j} (2k_i + 1)(2k_i + 1) \]  

(9.46)

with \( \gamma = 1 \) for \( \Delta \Omega = 0 \) and \( \gamma = 1/4 \) for \( \Lambda = \pm 1 \). The factor following \( \gamma \) is a \( 6j \) symbol (Edmonds 1957).

Calculation of the line-strength factors is more complex if the coupling scheme changes in the transition sequence. The coupling may change with the rational quantum number, \( j \), or vibrational quantum number, \( v \). Line-strength factors for intermediate coupling schemes are given by Kovacs (1969).

Perturbation of electronic wave functions will also cause the line-strength factors to deviate from those of well-defined coupling cases. Calculations of the line-strength factors of perturbed levels require the knowledge of the perturbed wave function

\[ |\psi\rangle = \sum_k c_k |\psi^k\rangle \]  

(9.47)

with \( |\psi^k\rangle \) being the unperturbed wave functions of those states
that couple. The mixing coefficients are $c_k$. All $|\psi_k\rangle$ values must have the same angular momentum, $j$. The line-strength factor then reads

$$S_{l,l'} = \sum_{k} c_k^2 \langle \psi_k^* \parallel D_l \parallel \psi_k \rangle = \sum_{k} c_k^2 S_{l,l'}^k$$

(9.48)

In most cases, a linear combination of wave functions from only two states is sufficiently accurate for the description of perturbed states.

Finally, the apparent line-strength factor may be affected by partially resolved transitions, such as hyperfine components or spin multiplets with splittings $\Delta \omega_{sp}$, underlying a spectral absorption or emission feature. The effective line-strength factor for levels involving the set of quantum numbers $a$ and $b$ is then given by the weighted average

$$S_{a,b} = \sum_{a} \frac{1}{g_a} S_{a,b} F_a$$

(9.49)

with $F_a = \int f(\omega) L_a(\omega) d\omega$ [see equation (9.28)] for laser-induced absorption, but $F_a = 1$ for spontaneous emission. The sum is over the quantum numbers of unresolved states and $f(\omega)$ and $L_a(\omega)$ are the spectral energy density distribution function, equation (9.24), and the Lorentzian line shape, equation (9.20), respectively. The statistical weight of level $a$ is $g_a$.

$F_a$ depends on the line shapes and line positions of the transitions involved, as well as in the spectrum of the laser. The level separation may be smaller than, similar to, or larger than the experimental line width $\gamma_{\text{exp}}$. For $\Delta \omega_{sp} \gg \gamma_{\text{exp}}$, the transition frequencies under consideration are well resolved and the line-strength factors for individual transitions can be determined. For $\Delta \omega_{sp} \ll \gamma_{\text{exp}}$, the quantum numbers of the unresolved states are irrelevant. As an example, consider a $^3\Sigma - ^1\Sigma$ $P$-transition with unresolved spin states (Fig. 9.4). In this case, the line-strength factors are (Kovacs 1969)

$$S_{k+1/2,k-1/2}^0 = \frac{\left[\frac{k+1}{2}\right]^2 - \frac{1}{4}}{k + \frac{1}{2}}$$

$$S_{k+1/2,k-1/2}^0 = \frac{\left[\frac{k-1}{2}\right]^2 - \frac{1}{4}}{k - \frac{1}{2}}$$

$$S_{k+1/2,k-1/2}^2 = \frac{\left[\frac{k-1}{2}\right] + 1}{4\left[\frac{k-1}{2}\right] \left[\frac{k+1}{2}\right]}$$

(9.50)

and $g_e = 1/2$. According to equation (9.49) the averaged line-strength factor for spontaneous emission is

$$S_{a,b}^0 (^3\Sigma - ^1\Sigma) = \frac{1}{2} (S_{a,b}^0 + S_{a,b}^0 + S_{a,b}^0) = k$$

(9.51)

which is identical to the line-strength factor of a $^1\Sigma - ^1\Sigma$ transition. The same formulas would apply for $^1\Sigma - ^1\Sigma$ transitions with unresolved hyperfine structure caused by a nuclear spin of $I = 1/2$. 

Figure 9.4  Level diagram for a $^3\Sigma - ^1\Sigma P$ transition.
9.1.1.6 Angular Distribution of Spontaneous Emission. The angular distribution of the spontaneous emission is of crucial importance to the analysis of laser-induced fluorescence data from molecular beams. This is because the spatial distribution of the fluorescence depends on the orientational quantum number \( m \), as well as on its change \( \Delta m \) in the course of the optical transition. Furthermore, light is collected only from a solid angle \( \Omega < 4\pi \).

The angular emission probability of a photon with circular polarization \( \sigma = \pm 1 \) in the direction \( \hat{k} \), following a molecular transition \( \Delta m = \pm 1, 0 \) is given by

\[
P_{\text{em}}(\Delta m, \sigma, \hat{k}) = \frac{3}{8\pi} |D^{\Delta m, \sigma}_{\text{em}}(\hat{k})|^2
\]  

(9.52)

with \( \hat{k} \) measuring the angle relative to the direction of the axis along which \( j \) is quantized. The matrix elements are given by

\[
D^{\Delta m, \sigma}_{\text{em}}(\hat{k}) = \begin{pmatrix}
\frac{1}{2} (1 + \cos \hat{k}) & \frac{1}{\sqrt{2}} \sin \hat{k} & \frac{1}{2} (1 - \cos \hat{k}) \\
\frac{1}{\sqrt{2}} \sin \hat{k} & \cos \hat{k} & \frac{1}{\sqrt{2}} \sin \hat{k} \\
\frac{1}{2} (1 - \cos \hat{k}) & -\frac{1}{\sqrt{2}} \sin \hat{k} & \frac{1}{2} (1 + \cos \hat{k})
\end{pmatrix}
\]  

(9.53)

The angular part of the spontaneous emission probability summed over \( \sigma = \pm 1 \) reads

\[
\sin^2 \hat{k} \quad \text{for} \ \Delta m = 0
\]  

(9.54)

and

\[
(1 + \cos^2 \hat{k}) \quad \text{for} \ \Delta m = \pm 1
\]  

(9.55)

9.1.1.7 Level-to-Level Transition Probability. The Einstein coefficients \( B \) for absorption induced by unpolarized isotropic light and for the total emission rate \( A \) are related by (see, e.g., Yariv 1975, Demtroder 1981)

\[
A = \frac{\hbar \omega^3}{4 \pi c^3} B
\]  

(9.56)

In the context of this chapter, the absorption processes induced by polarized light of well-defined direction of incidence \( \hat{k} \), as well as the spatial distribution of the spontaneous emission, are of interest.

The Einstein coefficients \( B \) for isotropic and unpolarized radiation of spectral energy density \( \rho(\omega) \) is related to the rate \( W_\text{f}(a, m, \Delta m, \hat{k}) \) [see equation (9.23) and equations (9.41) through (9.44)] for transitions from the \( m \) state of level \( i \) to state \( m + \Delta m \) of level \( f \) by

\[
B_\text{f} \rho(\omega) = \sum_a \int d\hat{k} \frac{1}{8\pi} \sum_{\Delta m} W_\text{f}(a, m, \Delta m, \hat{k})
\]  

(9.57)

The sum is over all relevant quantum numbers, \( a \). The spectral energy density averaged over all directions of propagation \( \hat{k} \) is

\[
\rho(\omega) = 2 \int d\hat{k} \rho(\omega, \hat{k})
\]  

(9.58)
Equation (9.58) includes integration over the full solid angle \( \Omega = 4\pi \) and summation over the two states of polarization. For isotropic unpolarized radiation

\[
\rho(\omega, \hat{k}) = \frac{1}{8\pi} \rho(\omega)
\]  

(9.59)

is valid. Combining equations (9.23), (9.41) through (9.44), and (9.57) results in

\[
B_{\theta\phi} = \sum_{\sigma} \int d\hat{k} \frac{1}{g_i \Delta m} \sum b_{\sigma} \rho(\omega)
\]  

(9.60)

where

\[
b_{\sigma} = \frac{\pi}{h^2 \varepsilon_0} \frac{\mu^2 F_\sigma}{D_{\sigma}(\varepsilon)} \left( \frac{J_i \Delta m}{m_i} \right)^2 \frac{1}{8\pi}
\]  

(9.61)

is the directional Einstein coefficient for absorption introduced by Stepanov and Gribkovski (1968) and used by Altkorn and Zare (1984). Here and later, the indices \( i \) and \( f \) have been omitted from the transition dipole moment to avoid confusion of the labels for the electronic states with the initial and final rovibrionic levels. The corresponding relation for spontaneous emission from level \( f \) to level \( l \) is

\[
a_{\rho}(m_i, \Delta m, \hat{k}, \sigma) = \frac{3}{8\pi} \frac{\omega_p^3}{\sum \omega_{\rho}^3 F_\rho} A_{\rho} F_\rho |D_{\Delta m, \sigma}^i|^2
\]

\[
\times \left( \frac{J_f \Delta m}{m_f} \right)^2 S_{\mu \nu}
\]  

(9.62)

If the Franck–Condon factors are zero except for emission frequencies into a small spectral range \( (\Delta \omega_p \ll \omega_p) \), the factor \( \omega_p^3/(\sum \omega_{\rho}^3 F_\rho)^{-1} \) approaches unity. It is easy to verify that

\[
\sum_{\sigma} \sum_{g_i \Delta m} \int d\hat{k} a_{\rho}(m_i, \Delta m, \hat{k}, \sigma) = A_f
\]

is valid. Equation (9.60), valid for isotropic unpolarized radiation, can now be written as

\[
B_{\theta\phi} = \frac{\pi}{3} \frac{\mu^2 F_\theta}{2J_f + 1} \frac{1}{S_{\mu \rho}} \rho(\omega)
\]  

(9.63)

where

\[
\sum_{m_i} \int d\hat{k} D_{\theta\phi}(\varepsilon) = \frac{8\pi}{3}, \quad \sum_{m_i \Delta m} \left( \frac{J_i \Delta m}{m_i} \right)^2 = 1,
\]

and \( g_i = 2J_i + 1 \) have been used.

The relation between molecular properties and the spontaneous transition rate is finally given by

\[
A_{\rho} = \frac{1}{3} \frac{\omega_p^3}{\pi \varepsilon_0 c} \mu^2 F_\rho \frac{1}{2J_f + 1} S_{\mu \rho}
\]  

(9.64)

The electronic lifetime \( \tau = \sum \tau_{\rho} A_{\rho}^{-1} \) is related to the transition dipole moment, \( \mu \), by

\[
\tau_f = \frac{1}{3} \frac{\mu^2}{h \varepsilon_0 c} \sum_{\rho} \omega_p F_\rho
\]  

(9.65)

where the difference in transition frequency to the accessible
rotational levels within the same vibrational state, \( v_i \) has been neglected to make use of the relation \((2j_f + 1)\sum_{j_f} S_{j_f} = 1\). Also, a transition dipole moment independent of the vibrational level has been assumed.

Combining equations (9.65) and (9.41) through (9.44) with equation (9.27) yields the final result

\[
W_{\ell}(m, \Delta m, \hat{k}) = 3 \frac{\pi c^3}{\hbar \sum_{\ell} \omega_{\ell} F_{\ell}} A_\ell F_\ell D_\ell(\hat{\ell})
\]

\[
\times \left( \begin{array}{c} j_i \ 1 \\ -m_i \ \Delta m \ m_f \end{array} \right) \frac{L_i^2}{c} \frac{L_f^2}{c} \frac{F}{\gamma} \quad (9.66)
\]

Equation (9.66) relates the level-to-level transition rate induced by a laser of intensity \( I \) and polarization \( \hat{\ell} \), propagating in the direction \( \hat{k} \), to the more readily available molecular properties \( A_\ell \), \( F_\ell \), and \( S_{\ell,\ell'} \). \( F \) specifies the overlap of the spectral energy distribution function of the laser and the molecular absorption profile, as given in equations (9.28) through (9.32). \( D_\ell(\hat{\ell}) \) depends on the laser polarization according to equation (9.43).

9.1.1.8 Magic Angle Arrangements. Conversion of laser-induced fluorescence intensity to level populations is easiest when the detection probability, \( D(i) \) [equation (9.1)], is independent of the orientational quantum number \( m \). Unfortunately, this is not true in general, because both \( E(i, f) \) and \( K(f) \) depend on \( m \). In the following, the \( j \) and \( m \) quantum numbers are given explicitly. Other quantum numbers that are irrelevant in this context are not shown.

The angular dependent part of the detection probability, \( D \), is given by the collection efficiency \( C(f, l) \) [equation (9.4)]. The latter is obtained by integrating the directional Einstein coefficient for spontaneous emission, \( a_\mu \) [see equation (9.62)] weighted by the efficiency \( G(\hat{k}_d - \hat{k}_s) \) of the collection optics. Here, the direction of photoemission, \( \hat{k}_s \), is measured relative to the direction of the axis of symmetry, \( \hat{k}_d \), of the detector Fig. 9.5. This leads to

\[
C(f, l) = A_f^{-1} \sum_{\Delta m, \alpha} \int a_\mu(m_i, \Delta m, \hat{k}_s, \alpha) G(\hat{k}_d - \hat{k}_s) d\Omega_{\hat{k}_s} \quad (9.67)
\]

which can be rewritten as

\[
C(f, l) = \frac{\omega_{f}^3}{\sum_{\ell} \omega_{\ell} F_{\ell}} \sum_{\Delta m, \alpha} F_{\Delta m, \alpha}^{P.R.Q} \quad (9.68)
\]

where

\[
F_{P.R.Q}^{\Delta m, \alpha} = \sum_{\Delta m, \alpha} \left( \begin{array}{c} j_f \ 1 \\ -m_f \ \Delta m \ m_i \end{array} \right) F_{\Delta m, \alpha} \quad (9.69)
\]

and

\[
F_{\Delta m, \alpha} = \frac{3}{8\pi} \int |D_{\Delta m, \alpha}(\hat{k}_s)|^2 G(\hat{k}_d - \hat{k}_s) d\Omega_{\hat{k}_s} \quad (9.70)
\]

contain all angular-dependent factors. The upper index of \( F_{P.R.Q}^{\Delta m, \alpha} \) indicates the type of optical transition, with \( P, R, \) and \( Q \) referring to \( j_f - j_i = +1, -1, \) and 0, respectively.

A specific detection configuration that eliminates the \( m \) dependence from the product \( E(i, f) K(f) \) in the limit of saturated excitation is discussed next. In this limit the excitation probability \( E(i, f) \) is either 0 or 1, depending, respectively, on whether or not...
the level-to-level transition probability is zero [see equation (9.66)], and the \( m \) dependence of \( D(i) \) is determined by the emission process alone. \( E(i,f) = 1 \) for all levels of \( m_i \) can be ensured for \( R \) transitions, if the laser power is sufficiently high.

The fraction of the fluorescence of circular polarization, \( \sigma = \pm 1 \), that is collected following a transition, \( \Delta m \), is given by equation (9.70) with the linear polarization \( \vec{e} \) of the excitation laser being the quantization axis. The angles between \( \vec{e} \) and \( \hat{k}_r \), \( \hat{k}_s \), and \( \hat{k}_a \), and \( \vec{e} \) and \( \hat{k}_a \) are labeled \( \theta' \), \( \xi \), and \( \gamma \), respectively. Evaluation of equation (9.70) with \( \cos \theta' = \cos \gamma \cdot \cos \xi - \sin \gamma \sin \phi \sin \xi \), \( d\Omega = \sin \xi d\xi d\phi \) and \( D_{0,\pm 1}(\theta') = 2^{-1/2} \sin \theta' \), \( D_{\pm 1,\pm 1}(\theta') = 2^{-1}(1 \pm \cos \theta') \) [see equations (9.53) and (9.54)], and assuming axial symmetry around \( \hat{k}_a \) \( [G(\hat{k}_a) \text{ depends only on } \xi] \), leads to

\[
F_{0,\pm 1} = \frac{1}{2} A - \frac{1}{2} BP_2(\cos \gamma) \quad (9.71)
\]

\[
F_{1,\pm 1} = \frac{1}{2} A + \frac{1}{4} BP_2(\cos \gamma) + \frac{3}{4} CP_4(\cos \gamma) \quad (9.72)
\]

and

\[
F_{-1,\pm 1} = F_{1,\pm 1} \quad (9.73)
\]

The quantities \( A \), \( B \), and \( C \) are determined by the detector geometry. They read

\[
A = \frac{1}{2} \int_0^\pi G(\xi) \sin \xi \, d\xi \quad (9.74)
\]

\[
B = \frac{1}{2} \int_0^\pi G(\xi)P_2(\cos \xi) \sin \xi \, d\xi \quad (9.75)
\]

and

\[
C = \frac{1}{2} \int_0^\pi G(\xi)P_4(\cos \xi) \sin \xi \, d\xi \quad (9.76)
\]

If \( G(\xi) = 1 \) within the solid angle \( \Omega_o \) but zero elsewhere, equation
(9.74) yields

\[ A = \frac{\Omega_p}{4\pi} \]  \hspace{1cm} (9.77)

Often the polarization of the fluorescence is not analyzed, and the sum over \( \Delta m \) [see equation (9.70)] is needed, this leads to

\[ F_0 = F_{0,+1} + F_{0,-1} = A - BP_2(\cos \gamma) \]  \hspace{1cm} (9.78)

\[ F_{\pm 1} = F_{\pm 1,+1} + F_{\pm 1,-1} = A + \frac{1}{2} BP_2(\cos \gamma) \]  \hspace{1cm} (9.79)

Evaluation of equation (9.69) with equation (9.78) and (9.79) yields the factor that determines the \( m \) dependence of the detection probability for the emitted photon, namely

\[ P^{p,k,q}(m_r) = \frac{1}{2j+1} \left[ A - B \frac{j(j+1)}{N^{p,k,q} Q} \left( 1 - \frac{m_r^2}{j(j+1)} \right) P_2(\cos \gamma) \right] \]  \hspace{1cm} (9.80)

with

\[ N^p = 2j(2j-1), \quad N^k = 2(j+1)(2j+3), \quad \text{and} \quad N^q = -2j(j+1) \]  \hspace{1cm} (9.81)

The most important result is the following. The count rate \( Z(j_r, m_r) \) of photons, originating from an individual \( m \) level and emitted on the \( f \rightarrow l \) transition is [see also equation (9.3)]

\[ Z(j_r, m_r) = A_r n(j_r, m_r) C(f, l) T(v_f) Q(v_f) \]  \hspace{1cm} (9.82)

The count rate

\[ Z(j_r) = \sum_{m_r} Z(j_r, m_r) \]

is proportional to the level population

\[ n(j_r) = \sum_{m_r} n(j_r, m_r) \]

only for the magic angle \( \gamma_M = 54.7^\circ \), where \( C(f, l) \) becomes independent of \( m_r \) [see equations (9.68), (9.70), and (9.80)].

As a specific example, consider the emission following a \( ^1\Sigma - ^1\Sigma \) transition. With \( S^f = f, \ S^g = 0 \) and \( S^k = j + 1 \) and \( G(\xi) = 1 \) for \( \xi < \xi_0 \) but \( G(\xi) = 0 \) elsewhere, equation (9.82) reads

\[ Z(j_r, m_r, ^1\Sigma \rightarrow ^1\Sigma) = TQ n(j_r, m_r) A_r F_{j_r} \times \left[ (1 - \cos \xi_0) - \frac{\cos \xi_0 - \cos^3 \xi_0}{2} \right] \frac{j_r(j_r + 1) - m_r^2}{(2j_r - 1)(2j_r + 3)} P_2(\cos \gamma) \]  \hspace{1cm} (9.83)

The index \( f \) refers to the electronically excited state. For \( \gamma = \gamma_M \), equation (9.83) reduces to

\[ Z(j_r, ^1\Sigma \rightarrow ^1\Sigma) = A_r n(j_r) F_{\Sigma f} \frac{\Omega_{\Sigma f}}{4\pi} T(v_f) Q(v_f) \]  \hspace{1cm} (9.84)

For the magic angle arrangement equation (9.80) or (9.83), ensures the proportionality of the fluorescence intensity to the population \( n(j_r) \) in the electronically excited state, not the ground state, \( n(j_r) \). The detection probability of ground state molecules in the level \( (j_r, m_r) \) becomes independent of \( m_r \) only if either the excitation occurs in the limit of saturation to ensure an excitation
probability $E(j, m) = 1$ for all $m$, or if, in the limit of weak excitation, unpolarized isotropic radiation is used. In the limit of saturation, the combined effect of optical pumping and spatial filtering by the collection optics may reintroduce an $m$ dependence of the collection probability (see section 9.2.3).

9.1.1.9 Summary. In the preceding text, the basic formulas for the analysis of laser-induced fluorescence data were summarized. The most important results are given in equations (9.66) and (9.80). The former equation relates the level-to-level transition rate with the electronic lifetime, Franck–Condon factors and line-strength factors as well as laser intensity, laser polarization and line width ($\gamma$) of the molecular transition, and width ($\gamma_s$) of the spectral energy distribution of the laser. The latter equation allows one to determine the collection efficiency for photons from a given transition. It shows that the collection efficiency is independent of the orientation of the molecule, provided the laser polarization makes an angle $\gamma_m = 54.7^\circ$ with the detector’s axis of symmetry. Determination of the overall detection efficiency of a molecule in the electronic ground state requires a more detailed analysis of the excitation processes.

9.1.2 Kinetics of Excitation

9.1.2.1 Introduction. The detection probability, $D(i)$, for a particle in the quantum state $i$ depends on molecular quantities, the properties of the laser, and the molecule–laser interaction time. In many cases of interest, the excitation probability is not small and equation (9.2) does not apply. Determination of $D(i)$ then requires solution of the appropriate system of rate equations. The rate equation approach for modeling the kinetics of spectroscopic transitions is justified when coherent phenomena that are rarely of interest for detection purposes can be neglected. Coherence effects can be neglected if either excitation conditions prevent the buildup of a well-defined phase of the wave functions for the different states involved or the system is given enough time to dephase (Hertel and Stoll 1977). Such conditions are met if the laser pulse ($\Delta t_L$) is long compared with the excited-state radiative lifetime, $\tau$, or if the fluorescence detector signal is integrated over times $\Delta t \gg \tau$. In the following, it is assumed that at least one of these conditions is fulfilled. Coherence phenomena will also be absent if the coherence time of the laser is short compared with the reciprocal of the stimulated emission rate. The latter occurs when lasers of broad bandwidths, compared with the bandwidth of the molecular transition, are used or if the laser exhibits large amplitude fluctuations.

Consider a three-level system (Fig. 9.6). Molecules in level 1 are excited to level 2 and return by radiative decay, either to level 1 or to one of a number of other states, which are summarized as level 3. Depending on the type of electronic transition, level 3 may include rotational levels in the same vibrational state as level 1. Unlike the kinetic scheme for excitation of molecules in the bulk, collisional relaxation, and in particular collisional transfer of molecules from level 3 back to level 1, is absent in the free flow regimen of molecular beams. Usually level 1 and level 3 are in the electronic ground state, and the $3 \rightarrow 1$ radiative decay rate is zero or sufficiently small to be neglected. Because of the low density of
particles in molecular beams, it is usually justified to neglect the rate of $3 \rightarrow 2$ absorption as well as $2 \rightarrow 3$-stimulated emission processes.

The molecules interact with the laser during the time interval $\Delta t$, and particles are transferred from level 1 to level 3. The excitation probability, $E(1, t)$, of equation (9.1) after the time, $t$, for excitation on the $1 \rightarrow 2$ transition is given by the fraction of particles removed from level 1, namely $E(1, t) = [n_2(t) + n_3(t)]/n_1(0)$. If the interaction time with the laser, $\Delta t$, as well as the photon collection time, $\Delta t_\phi$, are long compared with the electronic lifetime, $\tau$, $E$ is determined by

$$E(1, \Delta t) = \frac{n_3(\Delta t)}{n_1(0)} = N_3(\Delta t)$$  \hspace{1cm} (9.85)

The fractional population $N_3(\Delta t)$ is obtained from the rate equations, which can be solved analytically for several limiting cases of practical interest.

9.1.2.2 m-Level Dependent Rate Equations. In contrast with common assumption when interpreting laser-induced fluorescence data from molecular beams, isotropic orientation of molecular angular momenta is rarely ensured. The $1 \rightarrow 2$ transition probability depends on the $m$ quantum number [see equation (9.66)]. Therefore, a more complex level system must be considered (Fig. 9.7, level 3 is not explicitly shown). The set of rate equations reads

$$\begin{align*}
\dot{n}_1(j, m_1) &= -\Delta n_{12} W_{12}(j, j_2 m_1 m_2) + R_{21} \\
\dot{n}_2(j, m_2) &= +\Delta n_{12} W_{12}(j, j_2 m_1 m_2) - n_3(j, m_2) A_2 \\
\dot{n}_3(j, m_3) &= R_{23}
\end{align*}$$  \hspace{1cm} (9.86a)

with

$$\Delta n_{12} = n_1(j, m_1) - n_2(j, m_2)$$

$$R_{21} = \sum_{m_1} n_2(j, m_2) A_{21}(j, j_2, m_1 m_1)$$  \hspace{1cm} (9.86b)

and

$$R_{23} = \sum_{m_2} n_3(j, m_2) A_{23}(j, j_3, m_2 m_3)$$  \hspace{1cm} (9.86c)

Figure 9.7 Level system, including the degenerate $m$ levels. The third level (see Fig. 9.6) is not shown. The filled-in and open arrows correspond to $P$ and $R$ transitions, respectively. The relative transition probabilities are given explicitly for $j = 3$. 

\begin{itemize}
  \item \textbf{Figure 9.7} Level system, including the degenerate $m$ levels. The third level (see Fig. 9.6) is not shown. The filled-in and open arrows correspond to $P$ and $R$ transitions, respectively. The relative transition probabilities are given explicitly for $j = 3$.
\end{itemize}
$A_2$ is the total spontaneous emission rate of level 2. The sum in the last equation runs over the quantum numbers $a_i = (v_i, j_i, m_i)$ of all states accessible from level 2 except level 1.

The rate $W_{ij}(j_1, j_2, m_i, m_2)$ of individual $m_i \rightarrow m_2$ transitions [see equation (9.66)] depends on the type of electronic transition as well as on the state of polarization of the laser. Only the quantum numbers $j$ and $m$ are given explicitly, although $W_{ij}$ may depend on other quantum numbers as well. The system of rate equations (9.86a) through (9.86c) is rather complex since adjacent $m$ levels are coupled by the spontaneous emission. Successive pump cycles lead to coupling of all $m$ levels, and a numerical solution of equations (9.86a) through (9.86c) into a three-level system set of equations for each $m$ state are justified in many cases of practical interest.

9.1.2.3 $m$-Decoupling Approximations. A trivial type of uncoupling of the population of $m$ sublevels in level 1 occurs when $R_{21} \ll R_{12}$ is valid. Neglecting $R_{21}$ is justified if the excitation occurs on a transition with a small Franck–Condon factor $R_{12} \ll 1$.

Assuming $R_{21} = 0$ is equivalent to neglecting the repopulation of levels $m_1$ by spontaneous emission, and leads to a decomposition of the system of coupled equations into equations for a three-level system for each $m$ level. If spontaneous radiation back to level 1 is not negligible, equations (9.86a) through (9.86c) uncouple again if the spontaneous transition rates, for $m_2 \rightarrow m_1 = m_2 \pm \Delta m$ or for $m_2 \pm \Delta m = m_1$, are added to the rate for the $\Delta m = 0$ or $\Delta m = \pm 1$ process, for linear or circular polarization, respectively. Both approximations neglect spontaneous repopulation of the level $|m| = j$ for a $P$ transition.

Another commonly applied uncoupling approximation is to neglect any $m$ dependence of the transition rates. This approach seems unavoidable if the polarization of the laser is not well defined and information about the population of the $m$ sublevels is not available. The $m$-state dependence in equations (9.86a) through (9.86c) disappears when the sum over $m$ levels is taken for uniform population of $m_1$ states in level 1 and excitation occurs with unpolarized light. The solution of the $m$-uncoupled equations is given next. A more exact treatment of the process of optical pumping involving small $j$ is given by Bussert (1986) (see also Chapter 12, section 12.4.1).

9.1.2.4 General Solution of the Rate Equations. In many cases of practical interest, one of the $m$-decoupling approximations discussed in the preceding section is justified and equations (9.86a) through (9.86c) reduce to a set of three-level systems. For constant spectral energy density, $\rho(\omega)$, the fractional population $N_i(T)/\Sigma_i n_i(0)$ of level $i$, as a function of the dimensionless parameter $T = t/\tau$ that measures the time in units of the electronic lifetime $\tau$, is

$$
N_i(T) = \frac{1}{2} N_i(0) \left[ (1 + \beta^{-1/2}) e^{-\alpha T} + (1 - \beta^{-1/2}) e^{-\alpha T} \right] + N_i(0) (\epsilon + \delta) \beta^{-1/2} \left[ e^{-\alpha T} - e^{-\alpha T} \right] 
$$

(9.87a)

$$
N_i(T) = N_i(0) e^{-\alpha T} \left[ e^{-\alpha T} - e^{-\alpha T} \right] 
$$

(9.87b)
\[ N_2(T) = N_2(0) \left[ 1 + \delta \right] \theta^{-1/2} \left[ \frac{1}{\alpha^*} e^{-\alpha^* T} - \frac{1}{\alpha} e^{-\alpha T} \right] \\
+ N_2(0) \left[ 1 + (1 - \delta) \theta^{-1/2} \left( 1 - \frac{\theta}{\alpha^*} \right) e^{\alpha^* T} - \left( 1 - \frac{\theta}{\alpha} \right) e^{\alpha T} + N_2(0) \right] \\
(9.87c) \]

with
\[ \alpha^* = \frac{1}{2} \left( 1 + 2 \delta \pm \beta^{1/2} \right) \]
\[ \delta = \frac{A_{21}}{A_2} = F_{12} \left( \begin{array}{c} j_1 \ 1 \ j_2 \end{array} \right) S_{1\leftrightarrow 2} \]
\[ (9.87g) \]

The orientational dependence of the excitation kinetics is contained in the angular momentum coupling coefficient of \( W_{12} \) [see equation (9.66)] and \( \delta \). The parameter \( T \) sets the time scale for the interaction, while the transition from the linear to the saturated regime is basically controlled by the magnitude of \( \epsilon \cdot T \). The parameter \( \delta \) ranges from 0 to 1. A pure two-level system is described by \( \delta = 1 \). If the radiative lifetime is longer than the interaction time with the laser \( \Delta \), the population \( N_2(T = (\Delta T / \tau)) \) is not negligible. For \( T \gg \Delta T / \tau \), it is shared between level 1 and 3, according to the branching ratio for spontaneous decay, \( A_{21}/A_{23} \).

Actually, the molecules are exposed to a spatially or temporally changing laser field of spectral energy density, \( \rho(\omega, z, T) \). Instead of solving equations (9.86a) through (9.86c) numerically, it is appropriate, and computationally simple, to determine the level population by a stepwise analytical solution. This is done through iterative evaluation of equations (9.87a) through (9.87g). To determine \( N(T + \Delta T) \) from the previous solution \( N(T) \), the spectral energy, \( \rho(\omega, z, T) \), is replaced by its average value over a small interval, \( \Delta \omega \) or \( \Delta T \). As an example, the variation of the fractional population \( N(T) \) is shown in Fig. 9.8, for constant laser intensity, with the interaction beginning at \( T = 0 \) (see also Fig. 12.8). Figure 9.9 compares the excitation kinetics of rectangular and gaussian shape laser intensity profiles, \( \rho(\omega, z) \), for a branching ratio \( A_{21}/A_2 = \delta = 10^{-1} \). The total number of photons interacting with the molecules is the same in both cases, because the value of \( \int \rho(\omega, z(T)) \), along the flight path z(T), through the center of the laser beam, was chosen to be the same in both cases.

The molecules interact with the laser of rectangular shape from \( T = -5 \) to \( T = +5 \), where \( T \) measures the reduced flight time with respect to the center of the laser beam. For \( \epsilon \approx 10^{-1} \) and \( \epsilon \approx 10^{-3} \), the excitation probability, given by \( N_{1s} \), is nearly the same in both cases. For intermediate \( \epsilon \), the gaussian shape profile is slightly more effective because the interaction time is longer and the molecules undergo more pumping cycles.

Although the excitation probability, given by \( N_{1s}(T \rightarrow \infty) \), is similar in both cases, the spatial variation of the level population, in particular that of level 2, is significantly different. This is of

![Figure 9.8 Variation of the fractional level population](image)
crucial importance, when two-step processes are considered (see section 9.3.1).

A special case of particular importance is the excitation with a short laser pulse of length $\Delta t_s \ll \tau$. Electronic lifetimes are typically $\tau \approx 10^{-8}$ s, while lasers with pulse lengths shorter than $10^{-8}$ s are readily available. If the photon collection time, $\Delta t_c$, is long compared to $\tau$, coherence phenomena are not likely to affect the result. For $T \ll 1$, spontaneous emission to level 3 can be neglected. With $\delta = 1$, the parameters $\beta$ and $\alpha^*$ reduce to $\beta = (1 + 2\epsilon)^2$, $\alpha^* = \beta^{1/2}$, and $\alpha^- = 0$ and equations (9.87a), through (9.87g) reduce, for $N_i(0) = 1$, $N_3(0) = N_5(0) = 0$, and $T \gg 1$, to

$$
N_1(T) = \frac{1}{2}[(1 + \beta^{-1/2}) + (1 - \beta^{-1/2})e^{-\beta^{-1/2}T}]
$$

$$
N_2(T) = \epsilon \beta^{-1/2}[1 - e^{-\beta^{-1/2}T}]
$$

$$
N_3(T) = 0
$$

9.1.3 Detection of Flux and Density

9.1.3.1 Introduction. The detection probability of a molecule in a specific quantum state is determined, in addition to molecular properties, by the spectral energy density of the laser, the interaction time, $\Delta t_i$, with the laser, the residence time, $\Delta t_r$, of the molecule within the field of view of the collection optics, and the electronic lifetime, $\tau$.

It is important to establish whether the flux or the density of particles in a given quantum state is determined. Figure 9.10a shows a molecular beam of cross section $q$ and a laser of diameter $d_L$. For $\Delta t_s > d_L/\nu$, the conditions are equivalent to CW laser excitation; whereas $\Delta t_s < d_L/\nu$ usually holds for pulsed laser excitation. Here $\nu$ is the particle velocity. Photons are collected from an area of size $d_0 > d_L$. The detector signal, related to the laser-induced fluorescence from level 1,

$$
S(1) = \sigma(1)VE(1, \Delta t_i)K(2)E_p(\Delta t_r, \tau)
$$

is proportional to $N(1) = n(1)V$, that is, to the number of molecules in quantum state 1 in the sensitive volume $V$ of the detector that interact with the laser during the integration time of the detector, $\Delta t_i$, or the laser pulse duration, $\Delta t_s$. $S(1)$ is also proportional to the excitation probability $E(1, \Delta t_i)$, which depends on the laser power and $\Delta t_i$, the geometry-dependent part of the detection probability $K(2)$, given by equation (9.3), and the fraction $F_p(\Delta t_r, \tau)$ of photons emitted during $\Delta t_r$. The relevant volume is $V = q \Delta t_i \cdot \nu$ or $V = q \cdot d_L$ for CW or pulsed-laser excitation, respectively.

Two limiting cases are of particular interest. When the product $V E F_p$ is proportional to the velocity, $\nu$, $S(1)$ measures the flux of molecules. When the product $V E F_p$ is independent of $\nu$, the particle density is measured.

The fraction of photons emitted in the field of view of the detector, if $d_L \ll d_0$ (see Fig. 9.10a), is given by

$$
F_p(\Delta t_r, \tau) = (1 - e^{-\Delta t_r/\tau})
$$

For short electronic lifetimes $\tau \ll \Delta t_r$ and $F_p = 1$ results, and $F_p = \Delta t_r/\tau = d_0/\nu \tau$ is valid for $\tau \gg \Delta t_r$. In the latter case, the photon collection efficiency is velocity dependent. If the width of
the laser beam is larger than the extension of the field of view of the detector \((d_L \approx d_o, \text{ see Fig. 9.10b) ,} \) equation (9.90a) must be integrated according to \(\hat{F}_{p}(\Delta t_r, \tau) = (1/d_L) \int F(\Delta t_r, \tau) f(x) \, dx\) with \(\Delta t_r = x/\nu(t)\), and \(f(x)\) is the density distribution function. For uniform \(f(x)\) and the field of view centered on the laser axis, the result is (Schwenz and Parson 1980)

\[
\hat{F}_{p}(\Delta t_L, \tau) = -\frac{d_o}{d_L} \frac{\tau}{\Delta t_L} \left[ \frac{1}{\Delta t_L} \left( 1 - \exp \left( -\frac{d_o}{d_L} \frac{\Delta t_L}{\tau} \right) \right) \right] \\
\times \left[ \exp \left( -\frac{(d_L - d_o)}{2d_L} \frac{\Delta t_L}{\tau} \right) \right]
\]

(9.91)

9.1.3.2 Weak Excitation Limit, \(E < 1\). Operation in the linear regimen of excitation is ensured then \(W_{12} \cdot \Delta t_L < 1\). Linearization of the exponential terms in equations (9.87a) though (9.87g) leads, for \(t > \Delta t + \tau\), to

\[
N(t > \Delta t + \tau) = N(0) \left( 1 - \frac{A_{23}}{A_2} W_{12} \Delta t \right)
\]

(9.92)

\[
N(t > \Delta t + \tau) = 0
\]

\[
N(t > \Delta t + \tau) = N(0) \frac{A_{23}}{A_2} W_{12} \Delta t \]

The excitation probability \(E(1, \Delta t) = N(t(\Delta t))/N(0)\) is therefore given by

\[
E(1, \Delta t) = \frac{A_{23}}{A_2} W_{12} \Delta t
\]

(9.93)

For excitation with a CW laser \(\Delta t_L = d_o/\nu\) holds and \(E(1, \Delta t) \sim \nu^{-1}\) results. For excitation with a laser pulse of length \(\Delta t_L \ll d_o/\nu\), \(\Delta t_L = \Delta t_L\) is valid and \(E(1, \Delta t)\) becomes independent of the particle velocity. For small excitation probability with a CW laser \((W_{12} \cdot d_o/\nu \ll 1)\) and long lifetime \((\tau \gg \Delta t_r)\), the result is \(S(1) \sim n/\nu\) (Table 9.2) and neither flux nor density is recorded.

9.1.3.3 Saturation Limit, \(E = 1\). Saturation in a three-level system is achieved when \(N_1 = N(0)\) [see equations (9.87a) through (9.87g)]. In that case, \(S(1)\) is proportional to the particle flux, for CW excitation, if the electronic lifetime is sufficiently short \((\tau \ll \Delta t_r)\). Otherwise \((\tau \ll \Delta t_r)\) particle density is again detected. Pulsed excitation results in the detection of density \(n\) or \(n/\nu\) for short or long electronic lifetimes, respectively (see Table 9.2). Saturation is not easily achieved except for single-mode laser excitation of strong transitions (see, e.g., Guyer, Hüwel, and Leone 1983; Altkorn and Zare 1984; Hefter, Ziegler, Matthaeus, Fischer, and Bergmann 1986). There are several reasons for this. Saturation is most easily achieved for molecules crossing the laser beam near its center but not for those in the wings of the intensity profile. If the detector views the entire laser beam, numerical integration over the cross section of the laser beam is required to establish the average detection probability. If photons are collected only from the center of the laser beam, saturation is more easily observable but only a fraction of the laser power is used for the detection. Also, problems related to optical pumping upstream of the laser center are encountered (see section 9.2.3.3). At high laser intensity, multiphoton processes such as photodissociation or photoionization begin to compete with the spontaneous decay. This is a problem, in particular for broadband laser

Figure 9.10 Dimensions of the molecular beam, the laser beam, and the field of view of the collection optics that are relevant for the detection process.
Table 9.2 Detection Characteristics for Various Combinations of CW/Pulsed and Linear/Saturated Excitation of a Short/Long-Lived State

<table>
<thead>
<tr>
<th>Short Lifetime $\tau \ll \Delta t_p$</th>
<th>Long Lifetime $\tau \gg \Delta t_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW $\Delta t_L \gg \frac{d_L}{u}$</td>
<td>CW $\Delta t_L \gg \frac{d_L}{u}$</td>
</tr>
<tr>
<td>Pulsed $\Delta t_L \ll \frac{d_L}{u}$</td>
<td>Pulsed $\Delta t_L \ll \frac{d_L}{u}$</td>
</tr>
</tbody>
</table>

Weak excitation

$W_{12} \Delta t \ll 1$

Density $\frac{1}{u}$ Density $\frac{1}{u}$

Strong excitation

$W_{12} \Delta t \gg 1$

Flux Density $\frac{1}{u}$ Density

excitation, because only a small fraction of the laser power is used for bound–bound transitions but the entire power can be effective for bound-free transitions.

9.1.3.4 Two-Level Systems. A pure two-level system requires $A_{12} = 0$ (see Fig. 9.6). A famous example is the excitation of Na($3s \rightarrow 3p$) between the $F = 2$ and $F = 3$ hyperfine components. Another example is a homonuclear molecule with dominant $\Delta v = 0$ vibrational bands. For example, excitation on a $Q$ line of a $\Sigma^+ \rightarrow \Pi^-$ transition would result in $Q$-line fluorescence only, and a two-level system may be appropriate to describe the excitation kinetics.

In such cases, the fluorescence is of the same wavelength as the laser, and particular care must be taken to eliminate scattered light (see section 9.2.3.2). The number of fluorescence photons, $N_{ph}$, is given by

$$N_{ph} = \int_0^{\Delta t} n_2(t) A_2 \, dt$$

(9.94)

For weak excitation this leads to

$$\frac{N_{ph}}{n_1(0)} = W_{12} A_2 \Delta t_i$$

(9.95)

while excitation in the limit of saturation yields

$$\frac{N_{ph}}{n_1(0)} = \frac{1}{2} A_2 \Delta t_i$$

(9.96)

In the former case, the number of photons is proportional to $r^2$. In the latter, the number of photons may significantly exceed 1 (Düren, Hoppe, and Pauly 1976).

9.1.4 Detection of Internal State Populations

9.1.4.1 Relation between Population and Intensity. The population of a single rotational level with degenerate $m$ states is

$$n(j_i) = \sum_{m_i} n(j_i, m_i)$$

(9.97)
while the photon count rate induced by the laser is

\[ Z(j^\prime) = A_f \sum_{m_j} n(j, m_j) D(j, m_j) \quad (9.98) \]

where \( A_f \) is the total transition rate from the excited state. In general, it is not possible to accurately determine \( n(j) \), or the ratios \( n(j)/n(k) \), from the laser-induced fluorescence. Equation (9.98) factorizes in a population-related and detector-determined factor only if either the detection probability, \( D(j, m_j) \), is independent of \( m_j \), leading to

\[ Z(j^\prime) = A_f \left[ \sum_{m_j} n(j, m_j) \right] D(j) \quad (9.99) \]

or isotropic level population is ensured, yielding

\[ Z(j^\prime) = A_f \frac{n(j)}{(2j^\prime + 1)} \sum_{m_j} D(j, m_j) \quad (9.100) \]

In order to discuss these limiting cases, the detection probability \( D(j, m_j) \) is now inspected in further detail. According to equation (9.1), it is given by

\[ D(j, m_j) = \sum_{m_j} E(j, m_j; j^\prime, m^\prime) K(j, m^\prime) \quad (9.101) \]

which leads with

\[ n(j, m_j) = \sum_{m_j} n(j, m_j) E(j, m_j; j^\prime, m^\prime) \quad (9.102) \]

to

\[ Z(j^\prime) = A_f \sum_{m_j} n(j, m_j) K(j, m^\prime) \quad (9.103) \]

where \( n(j, m_j) \) can be obtained from the solution of the rate equations (9.87). Here, excitation to a single rotational level, \( j^\prime \), is assumed. For weak excitation probability, \( E \ll 1 \), the excited state population is

\[ n(j, m_j) = \sum_{m_j} n(j, m_j) W(j, m_j; j^\prime, m^\prime) \Delta t \quad (9.104) \]

which reduces, for isotropic population of the levels \( m_j \), to

\[ n(j, m_j) = n(j) \frac{\pi c^3}{\hbar} \sum_i \frac{A_f}{\omega_i^P F \rho} \frac{1}{2j^\prime + 1} \frac{I_{2j^\prime}^2}{I_{\gamma F}^2} F \Delta t \quad (9.105) \]

[see equation (9.66)]. The rate of collected photons is obtained from equations (9.3), (9.68), (9.103), and (9.68) and reads

\[ Z(j^\prime) = A_f \left( \sum_{m_j} n(j, m_j) F^P, n Q(m_j) \right) M(j^\prime) \quad (9.106a) \]

with

\[ M(j^\prime) = \frac{\sum_i \omega_i^P F \rho \rho T P Q f T \rho Q f T}{\sum_i \omega_i^P F \rho T P Q f T} \quad \frac{1}{2j^\prime + 1} \frac{S_{\mu \nu}}{\sum_i \omega_i^P F \rho T P Q f T} \quad (9.106b) \]

where \( T_P \) and \( Q_P \) are the transmission and quantum efficiency for photons emitted in the transition \( f \rightarrow l \). Combining equations
(9.106) and (9.105) gives the final result

\[ Z_{ji} = n_{ji} \frac{\pi c^2}{h} \sum_{j} \frac{A_{ij}}{\omega_p F_{pi}} \frac{I_{ji}}{c} \frac{F_{ji}}{\Delta t} \]

\[ \times \sum_{m_f} F_{piQ}(m_f) M_{ji} \]  

(9.107)

Depending on the actual experimental setup, equation (9.107) can be simplified significantly. If magic angle arrangement is used, the sum \( \sum_{m_f} F_{piQ}(m_f) \) reduces to \( \Omega_D/4\pi \), where \( \Omega_D \) is the solid angle from which photons are collected. If light from all rotational branches of a vibrational transition is detected, and the difference in transition frequency, \( \omega_p \), within one vibrational transition is neglected, the line-strength factor, \( S_{ji} \), disappears from equation (9.107), since [see equation (9.106b)]

\[ \sum_{r} \frac{1}{2l_f + 1} S_{rji} = 1 \]

where \( l' \) runs over the relevant rotational levels in a given vibrational state. If the difference in the transition frequency to the various vibrational levels can be neglected and all \( \omega_p \) values are replaced by \( \omega_{im} \), \( \omega_{im} F_{pi} = \omega_{in} \) results and the ratio \( \Sigma_{r} \omega_{pr} F_{ri} Q_{ri} / \Sigma_{r} \omega_{pr} F_{ri} \) reduces to \( \Sigma_{r} F_{ri} Q_{ri} \) because \( \Sigma_{r} F_{ri} = 1 \). Finally, if the product \( T_{ri} Q_{ri} \) of transmission and quantum efficiency is independent of the transition frequency, within the relevant range, \( M = T Q \) results. Equation (9.107) is valid for devices, such as photomultipliers, that measure photon flux. Other devices, such as bolometers or thermopiles measure the intensity. In the latter case, \( \omega_{pr} \) must be replaced by \( h \omega_{pr} \) because each photon contributes the energy \( h \omega_{pr} \) (see also section 9.2.4).

The ratio of the signal from two rotational levels, within the same vibrational level, is

\[ \frac{Z_{j1}}{Z_{j2}} = \frac{n_{j1} S_{jih}}{n_{j2} S_{jih}} \]  

(9.108)

The ratio of the signal from two vibrational levels is

\[ \frac{Z_{v1}}{Z_{v2}} = \frac{n_{v1} F_{v1} \sum_{r} \omega_{pr} F_{ri} T_{ri} Q_{ri}}{n_{v2} F_{v1} \sum_{r} \omega_{pr} F_{ri} T_{ri} Q_{ri}} \]  

(9.109)

provided all rotational levels contribute. Otherwise, the corresponding line-strength factors, \( S_{rji} \), must be included. In equation (9.109), \( \alpha = 3 \) if photon counts are recorded but \( \alpha = 4 \) if intensity is measured. If the excitation occurs on a saturated R transition with linear laser polarization, \( n_{j1} = n_{j2} \) is valid instead of equation (9.104), and the ratio of line-strength factors and Franck–Condon factors must be replaced by unity in equation (9.108) and equation (9.109), respectively. Furthermore, it must be decided, from the kinetics of the excitation, whether flux or density is detected (see section 9.1.3).

Spectroscopic studies of the high-density region close to the nozzle (see, e.g., Aoi, Opyrko, and Bernstein 1983; Aerts, Huisman, and Willems 1982, 1984) may be plagued by radiation trapping. If a major fraction of the fluorescence is emitted to low-lying thermally populated levels, the reabsorption probability of the photons may be high and the detection probability depends
strongly on the location in the expansion zone. Under such circumstances, cutoff filters should be used that transmit only light from transitions to thermally nonpopulated levels. Although a loss of signal will occur, the result is a uniform detection probability across the volume of interest.

A study of the effect of saturation on the laser-induced fluorescence has been made by Altkorn and Zare (1984). They consider an isotropic ensemble of molecules irradiated by linearly polarized light of a pulsed laser, the pulse width $\Delta t$, of which is short compared with the electronic lifetime, $\tau$. Thus, they are dealing essentially with a two-level system and complications resulting from population redistribution between $m$ levels by successive pump-decay cycles are not considered. Figure 9.11 shows the variation of fluorescence with reduced absorption probability $D = b_{12} \Delta t / h$ [$\Delta t / (h \Delta \nu)^3$ [see equation (9.61)] for the fluorescence polarization parallel ($I_\|)$ and perpendicular ($I_\perp$) to the laser polarization, as well as the average intensity $(I_\| + I_\perp)/2$. The dependence on molecular orientation and laser intensity is retained in the quantity $D$, but the overall magnitude of the excitation rate is canceled out. The solid lines are calculated using the appropriate directional Einstein coefficients given in equation (9.61). For comparison, the dashed line gives the solutions of the rate equations using the integrated Einstein coefficient in equation (9.60). For low excitation probabilities (see Fig. 9.11 inset), the difference is marginal. For strong excitations, however, deviations of the order of 30% may occur.

Molecules with their transition dipole moment aligned parallel to the laser polarization have the highest excitation probability. They contribute preferentially to $I_\parallel$. Therefore, the onset of saturation is observed earlier for $I_\parallel$ than for $I_\perp$. This is more pronounced for $Q$ excitation and emission because the transition dipole moment is parallel to $j$ and no averaging resulting from the molecular rotation occurs.

### 9.1.4.2 Boltzmann Plots. Determination of rotational-vibrational level population

\[ n(v, j) = n_0 f(v, j) \quad (9.110) \]

leads to information about collision processes in the expansion zone of the molecular beam (see, e.g., Treanor, Rich, and Gehm 1968; Bergmann, Hefer, and Hering 1978; Bennewitz and Buss 1978; Gallagher and Fenn 1979; Campbell and Muntz 1979; Martin, Maravic, and Huetz-Aubert 1979; Aerts et al. 1984a,b) and is important for the analysis of state-to-state scattering data (Bergmann, Hefer, and Witt 1980) (see also Chapters 2, 23, and 24). Under equilibrium conditions, the distribution function $f(j, v)$ factorizes as $f(j, v) = f(j) \cdot f(v)$ with

\[ f(j) = \frac{(2j + 1)}{Q_{\text{rot}}} e^{-E_{\text{rot}}(j) / kT_{\text{rot}}} \quad (9.111a) \]

\[ f(v) = \frac{1}{Q_{\text{vib}}} e^{-E_{\text{vib}}(v) / kT_{\text{vib}}} \quad (9.111b) \]

The partition functions $Q_{\text{rot}}$ and $Q_{\text{vib}}$ ensure the normalization $\Sigma_j f(j) = 1$ and $\Sigma_v f(v) = 1$, respectively. If levels up to large $j$ are populated, the rigid-rotor approximation [$E_{\text{rot}}(j) = B(j + 1)$] yields $Q_{\text{rot}} = B/kT$ (Herzberg 1950).
Figure 9.12 Boltzmann plot for the rotational level population of Na$_2$ in a supersonic beam. For $j \leq 10$, the population distribution is characterized by $T_{rot} = 28$ K. With respect to this temperature, an excess population is found for levels $j > 10$. [From Bergmann, Heeter, and Witt (1980).]

Significant deviations from equilibrium population distributions, however, are common in a molecular beam environment (see, e.g., Treanor et al. 1968; Bergmann et al. 1978; Campbell and Muntz 1979). The rotational level distribution may be different in different vibrational levels. Neither $n(u, j)$ for given $u$ nor $n(u) = \sum_j n(u, j)$ necessarily closely follows the population distribution given by equations (9.110) and (9.111). It is nevertheless convenient to refer to an approximate rotational or vibrational temperature determined from equation (9.111). The slope of $\ln\left(\frac{n(u, j)}{2j + 1}\right)$ versus $E_{rot}(u, j)$ or $\ln n(u)$ versus $E_{ vib}(u)$ reveals to what extent thermal equilibrium is established in the various degrees of freedom (see Fig. 9.12), since

$$\ln\left(\frac{2j + 1}{2j_1 + 1}\right)\frac{n(u, j_1)}{n(u, j_2)} = -\frac{1}{kT_{rot}} [E_{rot}(u, j_1) - E_{rot}(u, j_2)]$$  

$$\ln\frac{n(u_1)}{n(u_2)} = -\frac{1}{kT_{ vib}} [E_{ vib}(u_1) - E_{ vib}(u_2)]$$

The relation between the level population and the observed signal is given in equations (9.107) through (9.109). In most cases, it is sufficient to relate the ratio of level populations to the ratio of observed signals as given, for example, in equation (9.108) or equation (9.109).

The absolute value of particle density or flux for a given quantum state is difficult to measure, because $T$ and $Q$ of equation (9.3) are usually not well known. In most cases it is sufficient to calculate $n_0$ of equation (9.110) from elementary molecular beam theory (see Chapter 2), and to determine $f(j)$ and $f(u)$ of equation (9.111) from the ratio of observed signals.

9.1.5 Detection of Alignment

9.1.5.1 Introduction. Detection of molecular alignment is an experimental probe for angular momentum correlations in collision processes (Prisant, Rettna, and Zare 1981 and 1982). Experimental information on alignment is accessible because the transition moment, $\mu_\nu$, has a well-defined orientation in the molecular frame. For so-called parallel transitions, it lies along the
molecular axis of symmetry, perpendicular to \( j \) (examples are \( P \) and \( R \) transitions in a \( \Sigma-\Sigma \) band), whereas for perpendicular transitions it lies perpendicular to the axis of symmetry (examples are \( Q \) transitions in \( \Sigma-\Pi \) absorption bands) (see Fig. 12.14). The fluorescence emission of an aligned ensemble of molecules is polarized, and the intensity of laser-induced fluorescence depends on the direction of the laser’s linear polarization, \( \hat{e}_\alpha \).

It is convenient to expand the spatial distribution function, \( f(\vec{j}) \), defined by \( n(\vec{j}) = n_0 f(\vec{j}) \) in Legendre polynomials with the moments \( a_i \) (Sinha, Caldwell, and Zare 1974, see also Chapter 24)

\[
f(\vec{j}) = K \sum_i a_i P_i(\vec{j}) \tag{9.113}
\]

With \( K = 1/4\pi a_0 \), normalization is according to \( \int f(\vec{j}) \, d\Omega = 1 \), while \( K = 1/2 \) leads to \( \int f(\vec{j}) \, d(\vec{j}) = 1 \). Independent of the normalization constant \( K \), the weighted average of the Legendre polynomials, \( P_a \), is

\[
\langle P_a(\vec{j}) \rangle = \frac{\int f(\vec{j}) P_a(\vec{j}) \, d(\vec{j})}{\int f(\vec{j}) \, d(\vec{j})} \tag{9.114}
\]

From equations (9.113) and (9.114) it is easy to show that \( \langle P_a(\vec{j}) \rangle \) is related to the ratio of moments by

\[
\langle P_a(\vec{j}) \rangle = \frac{1}{2k + 1} \frac{a_2}{a_0} \tag{9.115}
\]

A commonly applied alternative representation of \( f(\vec{j}) \) uses multipole moments \( A_\alpha^{(a)} \), that are related to the Legendre moments of equation (9.113) by

\[
A_2^{(a)} = \frac{2 a_2}{5 a_0} \tag{9.116}
\]

and

\[
A_0^{(a)} = \frac{1}{9} \frac{a_4}{a_0} \tag{9.117}
\]

The latter equation, however, is only valid in the limit of large \( j \) (Greene and Zare 1982).

The experimentalist encounters two characteristically different situations: (1) the ensemble of molecules under investigation is in its electronic ground state, and alignment is inferred by interrogation with a polarized laser beam, or (2) a reaction or inelastic collision process leads to electronically excited species and the molecular alignment can be inferred from the analysis of fluorescence polarization. The intensity of the fluorescence of polarization, \( \hat{e}_\alpha \), induced by a laser of polarization \( \hat{e}_\alpha \) is given in the limit of weak excitation \( E \ll 1 \) [see equation (9.27)] by

\[
I(\hat{e}_\alpha, \hat{e}_\alpha) = K' n_0 \int_{-1}^{+1} f(\vec{j}) (\hat{e}_\alpha \cdot \hat{a}_\alpha)^2 (\hat{e}_\alpha \cdot \hat{a}_\alpha)^2 \, d(\vec{j}) \tag{9.118}
\]

where \( K' \) combines all other factors that relate population and intensity and that remain constant as \( \hat{e}_\alpha \) or \( \hat{e}_\alpha \) changes. For a parallel-transition with \( \mu \) in the plane of rotation

\[
\hat{\mu} = 1 - \hat{e} \hat{j} \tag{9.119}
\]
is valid, whereas for a perpendicular transition $\hat{\mu}$ is perpendicular to the plane of rotation, but parallel to $\hat{j}$, and

$$\hat{\epsilon}\hat{\mu} = \hat{\epsilon}\hat{j}$$  \hspace{1cm} (9.120)

holds. The product $\hat{\epsilon}\hat{\mu}$ can be expressed in terms of the Legendre polynomial $P_l$

$$(\hat{\epsilon}\hat{\mu})^2 = \frac{1}{3} (2P_3(\hat{\epsilon}\hat{\mu}) + 1)$$  \hspace{1cm} (9.121)

Because

$$\int_{-1}^{+1} P_k(\cos \theta)P_l(\cos \theta)d(\cos \theta) = \frac{2}{2l+1} \delta_{kl}$$  \hspace{1cm} (9.122)

it is obvious from equations (9.118), (9.121), and (9.122) that only the Legendre moments $a_2$ and $a_3$ of $f(\hat{j}\hat{\epsilon})$ can be determined (for further details, see Chapter 24). If excitation occurs at the saturation limit, $E = 1$, the excitation probability becomes independent of $(\hat{\epsilon}_s \cdot \hat{\mu}_s)^2$, and only the $a_2$ coefficient of equation (9.113) can be determined. Higher-order moments are accessible, in principle, from polarization measurements of laser-induced fluorescence when excitation occurs in the transition region from weak to saturated excitation (see section 9.1.5.5). A different method for the determination of all Legendre moments will be discussed in section 9.1.5.6.

The intensity of fluorescence, $I(\hat{\epsilon} \hat{\mu})$, of polarization $\hat{\epsilon}$ from an aligned ensemble of electronically excited emitters with distribution function, $f^*(\hat{j}\hat{\epsilon})$ is given by

$$I(\hat{\epsilon} \hat{\mu}) = Kn_s \int f^*(\hat{j}\hat{\epsilon})(\hat{\epsilon} \hat{\mu})^2 d(\hat{j}\hat{\epsilon})$$  \hspace{1cm} (9.123)

It is again obvious from equations (9.122) and (9.123) that only the second Legendre moment is accessible in such an experiment.

9.1.5.2 Moments from Chemiluminescence. The degree of fluorescence polarization is defined differently by different authors. From the observed fluorescence intensity, $I_\parallel$ and $I_\perp$, with the polarizer parallel or perpendicular to the laser polarization, respectively, Greene and Zare (1983) apply the most commonly used relation

$$\tilde{P} = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}$$  \hspace{1cm} (9.124)

while Johnson, Pease, and Simons (1984) use

$$\tilde{R} = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}$$  \hspace{1cm} (9.125)

The quantities $\tilde{P}$ and $\tilde{R}$ are related to the second Legendre moment of $f(\hat{j}\hat{\epsilon})$ by

$$\langle P_2(\hat{j}\hat{\epsilon}) \rangle = \tilde{R} = 2 \frac{\tilde{P}}{3 - \tilde{P}}$$  \hspace{1cm} (9.126)

for a $Q$ transition, whereas

$$\langle P_2(\hat{j}\hat{\epsilon}) \rangle = -2\tilde{R} = 4 \frac{\tilde{P}}{\tilde{P} - 3}$$  \hspace{1cm} (9.127)
is valid for a $\hat{P}$ or $\hat{R}$ transitions. Equations (9.126) and (9.127), together with equation (9.115), yield the Legendre moments ratio $a_2/a_0$.

These relations are valid under the assumption of incoherent population of $m_1$ levels. In the presence of coherence, significant deviations from the expected maximum degree of polarization have been observed (Vigué, Grangier, Roger, and Aspect 1981).

9.1.5.3 The Consequences of Kinematic Averaging. In most cases, the quantity of interest is not $f(\hat{J}\hat{Z})$ but the distribution function $f(\hat{J}\hat{Z})$ with respect to an axis in the center-of-mass frame, such as the relative initial velocity, $\hat{Z}$. The function $f(\hat{J}\hat{Z})$ is a convolution of $f(\hat{J}\hat{Z})$ with the distribution function $f(\hat{Z})$ of $\hat{Z}$, given by

$$f(\hat{J}\hat{Z}) = \int f(\hat{J}\hat{Z}) f(\hat{Z}) \eta(\hat{Z}) \mathrm{d}(\hat{Z})$$  

(9.128)

For a given experimental setup, $f(\hat{Z})$ can be determined by Monte Carlo simulation.

Prisant, Rettner, and Zare (1981) show that the alignment parameter $a_2$, is conveniently determined in a beam–gas-type of collision experiment. In comparison with a beam–beam experiment, the gain in signal is substantial, and the loss of sensitivity to the alignment parameter resulting from kinematic averaging is often surprisingly small. In the beam–gas arrangement, the distribution of relative velocities is cylindrically symmetric around the molecular beam axis. This leads to a factorization of equation (9.128). Written in the form of Legendre moments and using equation (9.114), the relation reads

$$\langle P_3(\hat{J}\hat{Z}) \rangle = \langle P_3(\hat{J}\hat{Z}) \rangle \langle P_3(\hat{Z}) \rangle$$  

(9.129)

If the distribution of $\hat{Z}$ is restricted to a very narrow cone around $\hat{Z}$, the Legendre moments of $f(\hat{J}\hat{Z})$ [see equation (9.113)] are, to a very good approximation, the same as for $f(\hat{J}\hat{Z})$, since $\langle P_3(\hat{Z}) \rangle \approx 1$. If, in contrast, the distribution function $f(\hat{Z})$ is isotropic, $\langle P_3(\hat{Z}) \rangle = 0$ results. In this case, the fluorescence is unpolarized even if a strong alignment exists in the center-of-mass frame, and no information about $f(\hat{J}\hat{Z})$ is experimentally accessible. For intermediate cases, the “blurring factor” is in the range $0 < \langle P_3(\hat{Z}) \rangle < 1$.

A detailed analysis of the kinematic blurring is given by Johnson et al. (1984) for beam–gas experiments with effusive and supersonic beams (Fig. 9.13). For typical experimental conditions $\langle P_3(\hat{Z}) \rangle$ depends only on the two dimensionless parameters $\rho$ and $S$. Here

$$\rho = \frac{\beta^2}{\alpha^2} = \frac{M_G T_B}{M_B T_G}$$  

(9.130)

is the square of the ratio of the width of the velocity distribution in the gas, $\alpha^2 = 2(kT_G/M_G)$, and in the beam, $\beta^2 = 2(kT_B/M_B)$, where $M$ is the molecular mass and $T$ the translational temperature. $S = u/\beta$ is the speed ratio of particles in the molecular beam, and $u$ is the flow velocity.

9.1.5.4 Determination of Legendre Moments from Laser-Induced Fluorescence. The preceding discussion, and in particular equations (9.126) and (9.127), are also valid for laser-induced

\[ \text{Figure 9.13 The kinematic blurring factor [see equation (9.129)] for the determination of molecular alignment in a beam gas arrangement. The width of the velocity distribution in the gas and beam is } \alpha \text{ and } \beta, \text{ respectively. The parameter is the speed ratio } S = u/\beta \text{ in the beam, where } u \text{ is the flow velocity.} \]
fluorescence. In this case, however, the Legendre moments of equation (9.113) apply to the alignment in the excited state. Because of the orientation dependence of the excitation process [see equation (9.66)], the excited state alignment is different from the alignment in the ground state and depends on the direction of polarization \( \mathbf{E} \) of the laser relative to the axis of symmetry.

Analysis of the fluorescence polarization for two orthogonal laser polarizations is needed to determine the Legendre moments \( a_2 \) and \( a_4 \) of ground state alignment. A detailed discussion of the procedure as well as the experimental problems involved is given by Dagdigian in Chapter 24, section 24.2.3, and will not be repeated here. The angular factors, excluding proportionality constants that remain unchanged when laser polarization is varied, are given in Table 24.3 as well as Table 1 of Altkorn and Zare (1984). Taking ratios of the observed intensities cancels the undetermined proportionality factors. The alignment coefficient can then be extracted from the resulting system of equations. Such experiments yield the moments of the distribution function \( f(\mathbf{J}) \), with respect to the \( \mathbf{Z} \) axis. The procedure, discussed in Section 9.1.5.3, must be applied to obtain the second moment of the distribution function \( f(\mathbf{J}) \) in the center-of-mass frame. This procedure, however, has so far been worked out only for the second moment. Determination of the moment \( a_2 \) of \( f(\mathbf{J}) \) is therefore limited to more favorable kinematic situations in which the “blurring” factor is estimated to be close to unity.

An interesting modification of the schemes discussed in this section that is applicable to differential scattering has been developed by Korving and co-workers to measure alignment of \( \text{Na}_2 \) and \( \text{I}_2 \) molecules in beams (Visser, Bekooy, van der Meij, de Vreugd, and Korving 1977). Instead of rotating the laser polarization and measuring the polarization of the fluorescence, the total fluorescence is monitored as the orientation of the molecules is changed by a magnetic field in the region between the scattering center and the detector (see Chapter 23, Fig. 23.19). Magnetic field \( B \) causes a precession of the molecular angular momenta. For an isotropic distribution of \( n(f) \) no change in the laser-induced fluorescence will be observed as the strength of the magnetic field changes. An anisotropic distribution leads to variation of fluorescence as the precession angle \( \beta \) increases. The precession frequency depends on the field strength \( B \) and the molecular magnetic moment, including the \( g_\text{e} \) factor. The precession angle depends, furthermore, on the interaction time with the field given by the interaction length, and thus varies with the molecular velocity. The relationship of the alignment coefficients \( a_2 \) and \( a_4 \) with the amplitude of fluorescence intensity modulation \( \Delta I/I_0 \) is given in equations (1) and (10) of Visser, Bekooy et al. (1977). The \( a_2 \) coefficient can be determined without knowledge of the field strength. The magnetic field does not even have to be homogeneous. The direction of the field experienced by the molecules, however, must be well defined. Determination of \( a_4 \) requires a more subtle analysis of the variation of fluorescence with field strength.

This technique was also applied to measure laser-induced alignment (Visser, van der Meij, Bekooy, Korving, and Beenakker 1977) and more recently to study collisional alignment in differential scattering (Treffers and Korving 1983). An apparent advantage of this approach is that no polarization analysis or
rotation of laser polarization is needed. The more complex dependence of the raw data on experimental parameters must be considered a disadvantage in comparison with the standard laser-induced fluorescence approach. In particular, the velocity dependence of the precession angle $\beta$ tends to rapidly damp the modulation as $\beta$ exceeds 180°; this leads to a corresponding averaging of the $n(f)$ distribution that reaches the detector. Although velocity averaging can be taken into account in the analysis, a loss of sensitivity results.

9.1.5.5 Moments from Saturated Fluorescence. Altkorn and Zare (1984) studied the relationship between fluorescence and laser intensity for nonisotropic distributions of $j$ (Fig. 9.14). The degree of polarization for small excitation probabilities, as well as the transition to the limit of strong excitation is characteristically different for isotropic (curve 1) and quadrupole-type ($a_2 \neq 0$; curves 2 and 3) distributions. A pure quadrupole distribution ($a_4 \neq 0$; curve 4) can be distinguished from the preceding at small reduced excitation probability, $D$, but it becomes indistinguishable from the isotropic distribution at large $D$ values. A pure hexadecapole distribution ($a_8 \neq 0$; curve 5) is indistinguishable from an isotropic distribution in fluorescence measurements, except for intermediate excitation probabilities. The sensitivity of the experimentally determined degree of polarization to the $a_6$ coefficient is very small, however, especially if $a_8$ is also nonzero.

Very recently, Jansen, Parker, and Stolte (1987) used computer algebra to derive analytical expressions that correlate experimental polarization data and alignment parameters. The results of these authors account in particular for the influence of saturation on determining alignment parameters. In their analysis, saturation effects are calculated without any prior knowledge of the orientational distribution, except for the assumption of cylindrical symmetry. Their results demonstrate that exact treatment is advisable even at relatively low saturation and in most cases can be carried out with only limited knowledge of the saturation conditions.

9.1.5.6 Determination of All Moments by Saturated Optical Pump and Probe Technique. It was realized many years ago (Ramsey 1955) that there is no fundamental reason why the Legendre moments, $a_k$ with $k > 4$ should be vanishing for an actual distribution function, $f(\mathbf{j})$, that results from a collision experiment (beam-beam or beam-surface inelastic or reactive collision). In the following, we discuss a technique (Hefter et al. 1986) that does allow the determination of all moments up to the order $2j$. It involves saturated optical pumping by two lasers. With the advent of powerful tunable pulsed lasers of Fourier-limited line widths, a large class of molecules should come within reach of this technique.

Figure 12.8 (Chapter 12) shows the variation of the transition probability with $m$, for excitation with linearly polarized light. For $|m| = j$, the transition probability is zero for P transitions but nonzero for R transitions. Figure 12.8 also shows the population distribution of $m$ levels for those molecules that have not been optically pumped to other vibrational–rotational states. The numbers apply to Na$_2$ molecules in the rotational level $j = 28$, which are pumped with a single-mode laser on the $v = 9 \rightarrow v = 0$,

![Figure 9.14](image_url)
\( A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+ \) transition at \( \lambda = 604 \text{ nm} \). With sufficiently high laser intensity and a high degree of linear polarization, all molecules can be pumped out of the given \( j \) level, when pumping occurs on an \( R \) line, whereas the population of all except the \( \left| m \right| = j \) levels will be depleted when saturated pumping occurs on a \( P \) line.

In a pump and probe arrangement, with both lasers exceeding the saturation intensity significantly, the excitation probability is \( E = 1 \) for all levels with \( W_0(m) \neq 0 \). With a detector in the magic angle configuration (see section 9.1.1.8) an \( m \)-independent collection efficiency of photons is ensured. Here, \( m \) and \( m' \) refer to the quantization axis \( \hat{\epsilon}_1 \) and \( \hat{\epsilon}_2 \), respectively (see Fig. 9.5). The angle between \( \hat{\epsilon}_2 \) and \( \hat{\epsilon}_1 \) is \( \beta \). The fluorescence signal for saturated \( P \) pumping and saturated \( P \) probing at the detector is given by

\[
I(\gamma_M, \beta) = K \sum_{|m| < j} n(m') | \beta \rangle (9.131)
\]

where \( K \) combines all the factors relating level population to intensity. The angle \( \beta \) on the righthand side of equation (9.131) is given for explicit reference to the quantization axis at angle \( \beta \) relative to \( \hat{\epsilon}_1 \). The population distribution

\[
f(j, m) = (2j + 1) \frac{n(m)}{n_j^0} (9.132)
\]

with respect to \( \hat{\epsilon}_1 \), prepared by the saturated \( P \) pumping from an isotropic population distribution, is given by

\[
f(j, m) = \begin{cases} 1 & \text{for } |m| = j \\ 0 & \text{for } |m| < j \end{cases} (9.133)
\]

Transformation of the population distribution of \( m \) levels into \( m' \) levels involves a rotation by the angle \( \beta \) between \( \hat{\epsilon}_1 \) and \( \hat{\epsilon}_2 \) according to

\[
n(m' | \beta) = \sum_m n(m) |d_{m,m}(\beta)\rangle |^2 (9.134)
\]

and leads, with equations (9.132) and (9.133), to

\[
n(m' | \beta) = \frac{n_j^0}{(2j + 1)} \left\{ |d_{m,m}(\beta)\rangle |^2 + |d_{m,-m}(\beta)\rangle |^2 \right\} \quad (9.135)
\]

Equation (9.135) implies isotropic distribution of molecular angular momenta upstream of the pump laser. The probe laser-induced fluorescence given by equations (9.131) and (9.135) is

\[
I(\gamma_M, \beta) = Kn_j^0 \frac{1}{2j + 1} \sum_{|m| < j} \left\{ |d_{m,m}(\beta)\rangle |^2 + |d_{m,-m}(\beta)\rangle |^2 \right\} (9.136)
\]

which can be rearranged with (Edmonds 1957)

\[
d_{m,m}(\beta) = \left( \cos \frac{\beta}{2} \right)^{2j}
\]

and

\[
d_{m,-m}(\beta) = \left( \sin \frac{\beta}{2} \right)^{2j}
\]

to give

\[
I(\gamma_M, \beta) = Kn_j^0 \frac{2}{2j + 1} \left[ 1 - \left( \cos \frac{\beta}{2} \right)^{4j} - \left( \sin \frac{\beta}{2} \right)^{4j} \right] (9.137)
\]

The factor of 2 accounts for the fact that \( n(|m|) \) is detected and
only alignment is considered. \( I(\gamma, \beta) \) has a minimum intensity \( I(\gamma, 0) = 0 \) and a maximum intensity \( I_{\text{max}} = I(\gamma, \pi/2) \) with

\[
I_{\text{max}} = Kn^{\beta} \frac{2}{2j + 1} \left[ 1 - \left( \frac{1}{2} \right)^{2j+1} \right] \tag{9.138}
\]

The normalized signal therefore reads

\[
\frac{I(\gamma, \beta)}{I_{\text{max}}} = \left[ 1 - \left( \frac{1}{2} \right)^{2j+1} \right] \left[ 1 - \left( \cos \frac{\beta}{2} \right)^{2j+1} - \left( \sin \frac{\beta}{2} \right)^{2j+1} \right] \tag{9.139}
\]

This result must be modified if the target molecules are aligned. The probe laser-induced fluorescence, in this case, depends not only on angle \( \beta \) between pump and probe laser polarization, but also on angle \( \theta \) of the pump laser polarization, \( \hat{e}_p \), relative to the molecular beam axis. Then, one has, instead of equation (9.137),

\[
I(\gamma, \beta, \theta) = Kn^{\beta} \frac{2}{2j + 1} f(j, j \mid \theta) \left[ 1 - \left( \cos \frac{\beta}{2} \right)^{2j+1} - \left( \sin \frac{\beta}{2} \right)^{2j+1} \right] \tag{9.140}
\]

The factor \( f(j, j \mid \theta) \) is proportional to the probability of finding the angular momentum \( j \) in the direction \( \theta \). It results from the transformation

\[
f(j, m = j \mid \theta) = \sum_{m'} f(j, m') |d_{m'}(\theta)|^2 \tag{9.141}
\]

of the distribution \( f(j, m') \) with respect to \( \hat{z} \) (see Fig. 9.5) to an axis parallel to \( \hat{e}_p \). This transformation accounts for the fact that only molecules in the level \( |m| = j \) are transmitted through the interaction region with the pump laser. For an isotropic distribution \( f(j, m') = 1 \) for all \( m' \), the result is \( f(j, j \mid \theta) = 1 \). Typical detector response curves are shown in Fig. 12.9 of Chapter 12.

The analysis of such curves yields the spatial distribution of \( j \) (see Hefter et al. 1986).

A more direct approach to molecular alignment measurements uses a combination of P pumping and R probing. For saturated R probing, in magic angle configuration, all levels \( m' \) are detected with uniform efficiency, and the signal following P pumping is given by

\[
I(\gamma, \theta) = 2Kn(m = j \mid \theta) \tag{9.142}
\]

Here, the angle \( \beta \) between \( \hat{e}_z \) and \( \hat{e}_p \) is irrelevant. Since \( |d_{m'}(0)|^2 = \delta_{m, m'} \), equations (9.132) and (9.141) lead to

\[
\frac{I(\gamma, \theta)}{I(\gamma, 0)} = \sum_{m'} f(j, m') |d_{m'}(\theta)|^2 \tag{9.143}
\]

Equation (9.143) relates the level population \( f(j, m') \) to the experimental data \( I(\gamma, \theta) \). The population distribution can be determined by inverting the system of linear equations (9.143) for selected angles \( \theta \), \( k = 0, 1, \ldots, j \) yielding \( f(j, m) = (R^T R)^{-1} R^T I(\gamma, \theta) / I(\gamma, 0) \). The elements of the matrix \( R \) are \( R_{m, n} = (2j + 1) |d_{m'}(\theta)|^2 \). On the other hand, the moments are determined by inserting equation (9.113) in equation (9.143) with \( j \hat{e} = \cos \theta \). After multiplication with \( P_\theta(\cos \theta) \) and integration over \( d(\cos \theta) \),

\[
\frac{A_\theta}{A_0} = (2k + 1) \frac{\int_0^\pi I(\gamma, \theta) P_\theta(\cos \theta) \sin \theta \, d\theta}{\int_0^\pi I(\gamma, \theta) \sin \theta \, d\theta} \tag{9.144}
\]
results. Equation (9.144) demonstrates that all Legendre moments of the distribution function $n_i(\theta)$ can be determined in principle from the experimental data $I(y_m, \theta)$. Two examples, the measurement of laser-induced alignment and the flow-induced alignment of the beam, are discussed in the following.

9.1.5.7 Examples. An experimental setup for the measurement of laser-induced alignment is shown in Fig. 9.15. Part of the pump laser beam is split off and interacts with the molecules further upstream. The polarization $\mathbf{e}_p$ of this laser beam is parallel to the molecular beam axis.

The auxiliary P pump (100 mW) prepares a highly aligned ensemble of molecules in the level $|m_p| = j$, where $m_p$ is defined with respect to $\mathbf{e}_p$. This ensemble is interrogated by the saturated P pump (130 mW), which acts as a filter. Only molecules in the level $|m| = j$ with respect to $\mathbf{e}_s$ are transmitted. The probability of finding a molecule in this level is equal to the probability of finding a molecule with angular momentum $j$ in the direction $\mathbf{e}_s$. The saturated R pump (120 mW) detects all molecules that survive the interaction with the probe laser in the given level $j$, independent of the quantum number $m$. Thus, the detector signal (Fig. 9.16) reflects the population of angular momenta prepared by the auxiliary laser. The level population $f(j, m^*)$ is determined from equation (9.143) by means of a least-squares fit procedure, subject to the constraint $f(j, m^*) \geq 0$ (Langbein and Matthias 1981). A sensitivity analysis of the least-squares procedure reveals that the signal-to-noise ratio is sufficient to determine all $f(j, m^*)$ values for $j \leq 6$. The results for selected $j$ levels are given in Table 9.3. The calculated distributions, $f(j, m^*)$, assuming pure $|m^*| = j$ selection by the auxiliary pump laser, and taking hyperfine coupling that mixes the population of $m$ levels into account, are also given in Table 9.3. Very good agreement with the experimental results is found.

The corresponding Legendre moments are given in Table 9.4 for $j = 4, 6,$ and 10. They are related to the level population by

$$a_k = \frac{2k + 1}{2} \sum_j f(j, m) \mu'_{km}$$

with

$$\mu'_{km} = \int P_k(\cos \theta) |d'_{km}(\theta)|^2 \sin \theta d\theta$$

which reduces to a product of Clebsch–Gordan coefficients

$$\mu'_{km} = (-1)^{j+m} \frac{2}{2k + 1} (jj - j | k0)(jm - m | k0)$$

All Legendre moments $a_k$ up to $l = 2j$ are needed to characterize the population distribution $f(j, m)$ completely. The moments determined from the experimental $f(j, m^*)$ of Table 9.4 are reliable only up to the order $l \leq j + 2$. Actually, the application of equation (9.144) is not appropriate in the case of a highly aligned distribution function, because the moments are numerically correlated unless the signal-to-noise ratio of the raw data is very high.

The detector response with a saturated R probe and a saturated P pump (see Fig. 9.17) shows pronounced flow-induced alignment. In contrast with the analysis of strong laser-induced alignment
(Fig. 9.16), the application of equation (9.144) rather than equation (9.143) is appropriate here because all \( m^* \) levels are populated and only the first few moments \( a_j \) are nonzero. The variation of the second moment, \( a_2 \), with \( j \) is shown in Fig. 9.18. For all levels, \( a_2/a_0 \leq 0.5 \) has been found (Hefter et al. 1986). All higher moments are negligible.

9.1.5.8 Other Techniques. Techniques have been developed for the experimental characterization of the distribution function \( f(q) \) other than those already discussed. Higher order moments can be determined not only by sequential interaction of several photons with a molecule (saturation), but also by interrogation by means of a multiphoton transition. Such concepts have been dealt with by Bray and Hochstrasser (1976), McClain and Harris (1977), Halpern, Zacharias, and Wallenstein (1980), and Bain and McCaffrey (1984). More recently, the number of experiments providing spectroscopic data about level population and alignment from \( 2 + 1 \) (two-photon absorption followed by resonant one-photon excitation) laser-induced fluorescence or from \( 2 + n \) multiphoton ionization is rapidly increasing. Analysis of such data has been treated by Dubs, Brühlmann, and Huber (1986) and in a detailed paper, written for the experimentalist, by Kummel, Sitz, and Zare (1986).

9.1.6 Detection of Velocities

9.1.6.1 Introduction. A careful analysis of molecular beam experiments requires the knowledge of the velocity distribution and angular divergence of the particles in the beam. Such data are needed to determine the mean collision energy as well as the distribution function of collision energies and the angular resolution in the center-of-mass frame. Velocity selection and detection by mechanical means are discussed in detail in Chapter

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**Table 9.3** Population of the Levels \( m \) of \( \text{Na}_2 \) from Data as Given in Fig. 9.16 and Using Equation (9.143) ("Exp")

<table>
<thead>
<tr>
<th>( j = 4 )</th>
<th>( j = 6 )</th>
<th>( j = 10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>Exp</td>
<td>Calc</td>
</tr>
<tr>
<td>4</td>
<td>0.310</td>
<td>0.305</td>
</tr>
<tr>
<td>3</td>
<td>0.096</td>
<td>0.101</td>
</tr>
<tr>
<td>2</td>
<td>0.047</td>
<td>0.058</td>
</tr>
<tr>
<td>1</td>
<td>0.044</td>
<td>0.028</td>
</tr>
<tr>
<td>0</td>
<td>0.009</td>
<td>0.016</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.020</td>
<td>( \chi^2 )</td>
</tr>
</tbody>
</table>

*The quality of the fit is measured by \( \chi^2 = r_{\text{max}}^2 \), where \( r_{\text{max}} \) is the maximum count rate, \( N \) is the number of data points, and \( M \) is the number of fit parameters. Calculated populations assuming initial pure \( |m| = j \) selection, and taking hyperfine mixing into account, are also given ("Calc"). For \( j = 28 \) the measured/calculated populations are 0.391/0.448 for \( m = 28 \), 0.069/0.049 for \( m = 27 \), and 0.040/0.006 for the sum of all \( m < 27 \). These data indicate that the optical pumping is not yet complete for a level with a rotational quantum number as large as \( j = 28 \). In this case, we have \( \chi^2 = 0.030 \).
13. Here the Doppler-shift technique and the time-of-flight (TOF) analysis involving lasers is discussed. More general aspects of the TOF technique are discussed in Chapter 14.

A complete description of the velocity distribution requires the inclusion of velocity components parallel ($v_\parallel$) and perpendicular ($v_\perp$) to the beam axis. Disregarding any correlation between parallel and perpendicular velocities, the complete distribution function reads

$$F(v_\parallel, v_\perp) = f_\parallel(v_\parallel)f_\perp(v_\perp) v_\perp \, dv_\perp \, dv_\parallel \, d\phi$$ (9.148)

with

$$f_\parallel(v_\parallel) = \frac{1}{\sqrt{\pi} \sigma_\parallel} \exp \left[ -\left( \frac{v_\parallel - \mu_\parallel}{\alpha_\parallel} \right)^2 \right]$$

$$f_\perp(v_\perp) = \frac{1}{\pi \sigma_\perp^2} \exp \left[ -\left( \frac{v_\perp}{\alpha_\perp} \right)^2 \right]$$ (9.149)

where $\alpha_{\parallel,\perp}$ measures the corresponding $e^{-1}$-width and $u$ is the flow velocity. The distribution function for $v_\parallel$ is obtained by integrating equation (9.148) over $v_\perp$. Typically the beam is well collimated by slits and only the central part of the velocity distribution contributes. Therefore

$$\int_0^{v_{\perp,\text{max}}} f(v_\perp)v_\perp \, dv_\perp \sim (v_{\perp,\text{max}})^2$$ (9.150)

since $f(v_\perp) \approx \text{const}$ for $v_\perp \ll v_{\perp,\text{max}}$. The maximum perpendicular component after the slit is $v_{\perp,\text{max}} = v_\parallel \tan \alpha$, where $\alpha$ is the collimation angle. This leads to

$$F_\parallel(v_\parallel) = C_\parallel \left( \frac{v_\parallel}{\alpha_\parallel} \right)^2 \exp \left[ -\left( \frac{v_\parallel - \mu_\parallel}{\alpha_\parallel} \right)^2 \right]$$ (9.151)

and

$$F_\perp(v_\perp) = C_\perp \exp \left[ -\left( \frac{v_\perp}{\alpha_\perp} \right)^2 \right]$$ (9.152)

where $C_\parallel$ and $C_\perp$ are normalization constants. Equations (9.151) and (9.152) are sufficiently accurate for most applications of interest here. Small deviations from this standard form in the wings of the distribution function have been found and are well

| Table 9.4 Legendre Moments for Saturated Laser-Induced Alignment Using Equations (9.143) and (9.145) for the Analysis of Experimental Raw Data ("Exp," see Fig. 9.16) and Determined from the Calculated Level Population Resulting from Hyperfine Mixing ("Calc")* |
|---|---|---|---|---|---|---|
| $j = 4$ | $j = 6$ | $j = 10$ |
| $m$ | Exp | Calc | Exp | Calc | Exp | Calc |
| $a_2$ | 1.48 | 1.48 | 2.33 | 2.45 | 3.33 | 3.42 |
| $a_4$ | 2.87 x 10$^{-1}$ | 2.41 x 10$^{-1}$ | 9.23 x 10$^{-1}$ | 8.41 x 10$^{-1}$ | 8.54 x 10$^{-1}$ | 8.99 x 10$^{-1}$ |
| $a_6$ | 2.18 x 10$^{-2}$ | 2.36 x 10$^{-2}$ | 1.59 x 10$^{-1}$ | 1.21 x 10$^{-1}$ | 1.65 x 10$^{-1}$ | 1.79 x 10$^{-1}$ |
| $a_8$ | -1.80 x 10$^{-3}$ | 1.81 x 10$^{-4}$ | 1.49 x 10$^{-2}$ | 1.26 x 10$^{-2}$ | 1.3 x 10$^{-2}$ | 2.4 x 10$^{-2}$ |
| $a_{10}$ | | | -7.4 x 10$^{-4}$ | 3.4 x 10$^{-4}$ | 3.9 x 10$^{-2}$ | 2.4 x 10$^{-2}$ |
| $a_{12}$ | | | -1.5 x 10$^{-4}$ | 1.3 x 10$^{-6}$ | 9.4 x 10$^{-2}$ | 2.4 x 10$^{-3}$ |

* The measured and calculated moments agree reasonably well up to the moments $l \leq j + 2$.

b All moments $a_l, l > 12$ are smaller than 10$^{-4}$. 
understood (Beijerinck, Kaashock, Beijers, and Verheijen 1983; Engelhardt, Lorenz, Bergmann, Mietzner, and Palczewski 1985; Haberland, Buck, and Tolle 1985).

9.1.6.2 The Doppler-Shift Technique. It was realized as early as in 1927 (Hogness and Franck 1927) that the Doppler shift of light is a suitable probe for the velocity of atoms or molecules resulting from photodissociation. Even an attempt to measure angular distributions by means of Doppler-shifted emission of Na(3P) atoms resulting from NaJ photodissociation has been reported (Mitchell 1928). Mitchell’s concept has been analyzed in more detail by Zare and Herschbach (1965). Recently, it has been widely used to study inelastic (Kinsey 1977b; Moskowitz, Stewart, Bilotta, Kinsey, and Pritchard 1984; see also Chapter 23) and dissociation processes (see e.g., Schmied, Böttner, Zacharias, Meier, and Welge 1979; Gerber and Möller 1985). The first systematic application to the study of molecular beams seems to be that of Muntz (1966), who observed Doppler-shifted emission of N₂ after electron excitation. This approach is plagued by a rather small signal level, because only the light emitted into a narrow cone can be used. The velocity resolution degrades with the increasing speed of the collection optics. Such problems are not encountered when total laser-induced fluorescence is monitored, as the laser frequency is tuned across an atomic or molecular resonance (Bergmann, Demtröder, and Hering 1975; Hertel, Hofmann, and Rost 1975). The Doppler-shifted absorption technique has become a routine technique for determining velocity distributions in beams.

Figure 9.19 shows the schematics of the experimental arrangements. The output from a single-mode laser is split into two beams. The two laser beams intersect the molecular beam in the same region, at θ₁^l = 90° and 0 ≤ θ^l ≤ 45°, respectively. The molecular absorption frequencies are shifted from the resonance at ω₀ according to

\[ \Delta \omega = k \nu \cos \theta^l \]  

(9.153)

The signal consists of a narrow absorption line at \( \omega = \omega_0 \) because of the beam with \( \theta^l_1 = 0 \) and a broader feature around \( \omega = \omega_0 \pm k \cdot \nu \cdot \cos \theta^l_1 \) (Fig. 9.20). The laser-induced fluorescence signal \( I(\omega) \) is a convolution of the velocity distribution, the molecular absorption profile \( L(\omega_0 - \omega', \gamma_N) \) and the excitation probability \( E \),

\[ I_{\nu^\parallel, \perp}(\omega) = K \int F_{\nu^\perp}(\nu^\parallel_0) E_{\nu^\perp}(\nu^\parallel_0) L(\omega_0 - \omega', \gamma_N) d\omega' \]  

(9.154)

with

\[ \nu^\perp_\nu = \frac{(\omega - \omega_0)}{k \cos \theta^l_\nu} \]  

(9.155)

The line width of the transition is \( \gamma_N \). The detection probability \( D_{\nu^\parallel, \perp}(\nu_0) \) is independent of \( \nu^\parallel \) for excitation near the saturation limit \( (E \approx 1; \text{see section 9.1.3}) \), but is proportional to \( \nu^{-1} \) for the more commonly used regime of weak excitation \( (E \ll 1) \). Because the interaction time with the laser is different for \( \theta^l_1 = 0 \) and \( \theta^l_1 \neq 0 \), \( E(\nu_0) \) is different for the two beams even if their power is identical. This fact is irrelevant, however, if \( E \ll 1 \) or \( E = 1 \) for both beams. Under typical experimental conditions, the width of \( I_0(\omega) \) and \( \gamma_N \) is of the order of 500 MHz and 10 MHz.

![Figure 9.17 Laser-induced fluorescence for Na₂ in the levels \( J = 1, 7, \) and 28, monitored by a detector in the magic angle configuration and operating on an \( R \) transition as the polarization of the pump laser that excites molecules on a \( P \) transition further upstream rotates (see equation (9.142)). The signal is proportional to the number of molecules with their angular momentum, \( J \), at an angle \( \theta \) to the molecular beam axis.](image)
respectively. In this case equation (9.154) shows that \( I_\lambda(\omega) \) is directly proportional to \( F(v_L) \cdot E(v) \) and the flux or density distribution is determined depending on the magnitude of \( E(v) \). The width of \( I_\lambda(\omega) \), on the other hand, is typically comparable with \( \gamma_N \) and the convolution with the Lorentzian absorption profile must be taken into account when \( F(v_L) \) is determined.

For some atoms the relevant level scheme may be approximated by a two-level system. Excitation of sodium on the transition \((3s, F = 2) \rightarrow (3p, F = 3)\) is an example. In this case, the average number of photons, \( n_{ph} \), emitted from an atom may be significantly larger than 1. It is proportional to the interaction time with the laser, and \( E(v) \sim 1/v \) results for low as well as high laser intensity. In this regimen, however, photon momentum transfer may alter the atomic velocity (Schieber, Walther, and Wöste 1972; Düren et al. 1976). In fact, the successful deceleration of atoms to very small velocities has been reported recently (Migdal, Prodan, Phillips, Bergeman, and Metcalf 1985).

The velocity resolution of the Doppler shift technique depends on the line width of the transition and the angular divergence of the beam. It is easy to verify from Fig. 9.19 that, for a given absorption line width and collimation angle, \( \alpha_c \), the velocity resolution is

\[
\Delta v = 2 \sin \alpha_c \tan \theta_L + \frac{\lambda}{v} \frac{\Delta v}{\cos \theta_L} \tag{9.156}
\]

The relative velocity spread, \( \Delta v / v \) (FWHM), resulting from the finite collimation angle is independent of \( v \), whereas the line width–related part decreases with \( v \). For typical parameters, \( \lambda = 500 \text{ nm}, v = 10^3 \text{ m/s}, \theta = 45^\circ, \Delta v = 2.0 \times 10^6 \text{ s}^{-1} \), and a collimation of \( 1:100 \), the terms of the right-hand side of equation (9.156) are of comparable magnitude and yield \( \Delta v / v = 2 \times 10^{-2} \).

Thus, the velocity distribution can be determined with reasonable accuracy for \( v / u \approx 0.1 \). The resolution of the Doppler shift technique may be impaired by closely spaced absorption lines, such as hyperfine components (Hertel et al. 1975). Despite the limitations, the technique offers, in conjunction with a compact mechanical setup, a convenient means of monitoring velocity distributions of atoms and molecules in individual quantum states.

A compact design is shown in Fig. 9.21. The laser beam is coupled to the detector with an optical fiber (see section 9.2.2). The light exiting the fiber is made parallel with a \( f = 10\text{-mm} \) lens. It crosses the molecular beam at \( 90^\circ \) and is reflected back with the help of two mirrors to cross the beam again at an angle of \( \approx 45^\circ \), before entering a beam dump. A lens collects the fluorescence and focuses it onto the surface of a fiber bundle that carries the light to a photomultiplier outside the vacuum chamber. Filters can be used to suppress scattered laser light if molecules are detected and part of the fluorescence is shifted to longer wavelength. Detection of ground state atoms may require careful spatial filtering of the light before it reaches the fiber bundle (see section 9.2.3).

9.1.6.3 Time-of-Flight Analysis by Optical Population Modulation. Time-of-flight analysis by means of optical population modulation overcomes most of the problems associated with the Doppler shift technique. It has a higher inherent velocity resolution and can be applied to molecules with a much higher density of absorption line. The population of a group of molecules.
Figure 9.20 Velocity distribution of Na$_2$ molecules in the level ($v = 0$, $j = 28$) measured by Doppler-shifted absorption. The narrow and broad peaks correspond to the distribution perpendicularly and parallel to the molecular beam axis. [Reproduced from Bergmann et al. (1975).]

In a given quantum state can be depleted or enhanced by optical means in a well-defined area downstream of the nozzle. The time variation of the modulation is given by the gate function $G(T)$ of width $\tau_g$. The labeled group of molecules spreads out in space according to the velocity distribution $F(v)$ and is detected further downstream after a flight path of length $L$. The signal is given by

$$S(t) = NL\int_0^t G(T)D\left(\frac{L}{L + \tau - T}\right)(t + \tau - T)^{-2}d\tau \, dT$$

(9.157)

In writing equation (9.157), $v = L/t$ and $dv = (L/t^2)dt$ have been used. The second integration is over the response time $\tau_g$ of the detector. $D(L/t)$ is the detection efficiency that may or may not be velocity dependent.

It is common to assume the functional form of the velocity distribution to be given by equation (9.151) and to determine the parameters $\alpha$ and $\mu$ by means of a least-squares fit to the observed signal. Using population modulation by optical means, it is easy to ensure $\tau_g \ll L/t$ and $\tau_g \ll L/t$. Then equation (9.157) reduces to

$$S(t) = CL\tau_g \frac{1}{\tau_g^2} F\left(\frac{L}{L + \tau - T}\right)$$

(9.158)

and the velocity distribution is proportional to $i^2 S(t)/D(L/t)$. The first application of this concept to molecular beams involving optical modulation seems to be that of Sungur and Théobald (1974), who used a Stark modulation technique to switch a particular quantum state of a molecule in and out of resonance with an RF field. In their case, $\tau_g$ was comparable to the average flight time and they obtained $F(v)$ by deconvolution of equation (9.157).

Laser optical pumping has been applied to population modulation by Gaily, Rosner, and Holt (1976), Bergmann, Heftner, and Hering (1976), Bergmann et al. (1978), as well as Kroon, Beijerinck, and Verster (1981). The schematics of the setup are shown in Fig. 9.22. Two laser beams from the same source cross the molecular beam at right angles at $A$ and $B$. The laser

Figure 9.21 A compact design for Doppler-shift velocity measurements. The laser beam crosses the flight path of the molecules at 90° and approximately 45°. The laser-induced fluorescence is collected by a retroreflector and a high-speed lens.
frequency is tuned to a particular transition frequency. Molecules interacting with the pumping beam at A are optically pumped out of the given quantum state, and the fluorescence observed at B decreases correspondingly. Interruption of the pump laser beam for a short time, $\tau_c$, of the order of $10 \mu s$ by electrooptical techniques or by a rapidly rotating disk that blocks the laser beam in the focus of two identical lenses, interrupts the optical pumping. Thus, the "optical shutter" for molecules in the given quantum state is "open" for the time $\tau_c$. The fluorescence at B is stored and signal averaged using a multiscaler. It reflects the time-of-flight distribution of molecules in this particular state. In fact, both $u$ and $\alpha_q$ have been found to vary significantly with the internal energy of the molecule (Bergmann et al. 1978). This technique has several distinct advantages. Mechanical interference with the beam and skimmer or collimating slits is avoided and the pumping can occur close to the nozzle. A large cross section of the molecular beam can be pumped when a cylindrical lens of appropriate focal length is used to focus the laser beam at A. The "optical shutter" opens instantaneously across the molecular beam, and the gate function, $G(t)$, can be made nearly rectangular in shape. With $v_i = 1000 \text{ m/s}$, $\tau_c = 10 \mu s$, and $L = 50 \text{ cm}$, the average flight time is $500 \mu s$ and equation (9.158) can be applied.

**Figure 9.22** (a) Schematic of the experimental arrangement for time-of-flight velocity analysis with internal state selection. The population in a given level is depleted by optical pumping at A. Interruption of the laser for a short time allows a group of molecules in the given level to pass through the interaction zone. They are detected at B, where they arrive at different times depending on their velocity. (b) Time-of-flight spectra of Na$_2$ molecules in the levels $(v = 3, j = 43)$ and $(v = 0, j = 28)$ and of sodium atoms. The particles emerge from a source at a temperature $T_0 = 1020 \text{ K}$ through a 200-$\mu$m nozzle. [Reproduced from Bergmann et al. (1978).]
It is not necessary to deplete the population in the given state fully. Any fractional depletion of the level population will give a response at the detector, from which $F(v_b)$ can be determined. Saturated optical pumping is advisable, however; otherwise, the transmission of the shutter becomes velocity dependent. If the pump or probe laser beam does not intersect the molecular beam at right angles, a $v_b$ dependence in the pump or probe process is introduced, and the observed time-of-flight spectrum will be distorted.

Another possible approach, mechanical chopping of the laser beam and state-selective laser detection, is discussed by Pasterнак and Dadigian (1977). They use a pulsed laser for detection and determine the flight time from the delay between the time a pulse of particles passes through a chopper slit and the time the laser fires.

### 9.2 Experimental Components

#### 9.2.1 Propagation of Laser Beams

Imaging and focusing are routine procedures in optical detection methods. Geometric optics treatment of the propagation of light waves is justified if diffraction phenomena are not important. Focusing of laser beams invariably requires more refined treatment. Some basic formulas are summarized next.

#### 9.2.1.1 Gaussian Beams.

The radial variation of the amplitude of the fundamental cavity mode has the gaussian profile (Yariv 1975)

$$E(z, r) = E_{r, 0} e^{-r/(w_0^2)} \quad (9.159)$$

where $z$ and $r$ measure the distance parallel and perpendicular to the direction of propagation, respectively. The amplitude at $r = 0$ is $E_{r, 0}$, and $w_0$ is the $e^{-1}$ radius at $z$. The variation of the beam waist $w(z)$ with $z$ is given by

$$w(z) = w_0 \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{1/2} \quad (9.160)$$

where $w_0$ is the minimum beam waist at $z = 0$ and $z_0 = (\pi/\lambda) w_0^2$.

For $z = z_0$, the waist has increased to $w(z_0) = \sqrt{2} w_0$. For $z \gg z_0$, equation (9.160) yields the angle of divergence, $\theta_0$, for the direction of propagation at $r = w(z)$

$$\tan \theta_0 = \frac{\lambda}{\pi w_0} \quad (9.161)$$

Equation (9.161) is a fundamental equation relating the far field angle of divergence and the size of the minimum waist. The minimum focal waist diameter for a beam of light with wavelength $\lambda$ and a lens of diameter $D$ and focal length $f$ is achieved when $2w_0 = D$ at the position of the lens. For $z \gg z_0$, the divergence is

$$\tan \theta_0 = \frac{2f \cdot \lambda}{\pi D} \quad (9.162)$$

The radius of curvature $R_e$ of the wavefront is given by

$$R_e = z_0 \left( \frac{\lambda}{z_0} + \frac{z_0}{z} \right) \quad (9.163)$$
A plane wavefront \((R_e = \infty)\) is observed for \(z = 0\), whereas a spherical wave \((R_e = z)\) results for \(z \gg z_0\).

For a cavity of cylindrical symmetry, the amplitude distribution of a laser mode other than the fundamental one is described by Laguerre polynomials. The waist and far field divergence angle of higher-order modes is related to the fundamental mode by (Kleen and Müller 1969)

\[
\omega_m = (m + 1)^{1/2} \omega_0 \quad (9.164a)
\]

\[
\theta_m = (m + 1)^{1/2} \theta_0 \quad (9.164b)
\]

where \(m\) is the order number of the mode.

The power of a gaussian beam for \(r \leq R_0\) is given by

\[
I(z, R_0) = \frac{1}{2 \pi \epsilon_0 c} \int_0^{2\pi} \int_0^{\infty} E^2(z, r) r dr d\phi \quad (9.165)
\]

Evaluation of equation (9.165) with equation (9.159) shows that 86 or 99.9% of the total power is concentrated within \(r \leq \omega_x\) or \(r \leq 2\omega_x\), respectively. For \(r = \omega_x\) the local intensity is 14% of the maximum value at \(r = 0\). To reduce the level of scattered light and avoid intensity loss, the diameter \(d_A\) of collimating apertures should be at least \(d_A = 3\omega_x\).

9.2.1.2 Propagation of Gaussian Beams. The transformation of a light ray, propagating at the distance \(d_a\) with an inclination angle, \(\alpha\), relative to the optical axis is given by (Kogelnik and Li 1966; Yariv 1975)

\[
\begin{pmatrix}
    d_2 \\
    \alpha_2
\end{pmatrix} =
\begin{pmatrix}
    A & B \\
    C & D
\end{pmatrix}
\begin{pmatrix}
    d_1 \\
    \alpha_1
\end{pmatrix} \quad (9.166)
\]

Each optical element has its characteristic transformation matrix.

For propagation over a distance, \(L\), in empty space \(A = 1, B = L, C = 0,\) and \(D = 1\), while transformation by a lens of focal length \(f\) leads to \(a = 1, B = 0, C = 1/f,\) and \(D = 1\).

The properties of a gaussian beam are uniquely described by the complex beam parameter \(q\), defined by

\[
\frac{1}{q} = \frac{1}{R_e} = \frac{\lambda}{2 \pi \omega^2} \quad (9.167)
\]

It can be shown (Yariv 1975) that the complex beam parameter transforms, according to the so-called ABCD-law, as

\[
q_2 = \frac{Aq_1 + B}{Cq_1 + D} \quad (9.168)
\]

The real and imaginary parts of \(q_2\) yield \(R_e\) and \(\omega_x\) of the transformed beam, respectively. The gaussian beam properties at the distance \(g\) from a lens of focal length \(f\) are transformed to the properties at the distance \(b\) at the other side of the lens by consecutive application of the three operations: propagation in free space with \(L = g\), transformation by the lens, and propagation in free space with \(L = b\). Matrix multiplication yields the complete transformation matrix and leads to

\[
q_2 = \frac{(1 - b/f)q_1 + g + b(1 - g/f)}{(-1/f q_1 + 1 - g/f)} \quad (9.169)
\]
The transformation of the minimum beam waist is of particular interest. For \( z = 0 \), the complex beam parameter reduces to

\[
q = i \frac{\pi \omega_0^2}{\lambda}
\]  

(9.170)

and equation (9.169) leads to

\[
(g-f)(b-f) = f^2 - f_0^2
\]  

(9.171)

with \( f_0 = (\pi / \lambda) \omega_{01} \omega_{02} \) and

\[
\omega_{02}^2 = \omega_{01}^2 \frac{b-f}{g-f}
\]  

(9.172)

For \( f_0 \ll f \), equation (9.171) is identical to the corresponding equation in geometrical optics. Otherwise, the position of the minimum waist of the image of a gaussian beam is not exactly at the location predicted by geometrical optics.

9.2.2 Optical Fibers

9.2.2.1 Introduction. In the traditional experimental setup, laser beams are steered from the laser to the molecular beam apparatus with the help of reflective surfaces such as mirrors or internally reflecting prisms. Although this approach is the only feasible technique for high-power pulsed lasers, it has several distinct disadvantages. Unless very high quality optical elements, firmly mounted on a solid base, are used, vibrations of the mirrors introduce pointing instabilities of the beam. Intensity loss also results because the reflectivity of surfaces is less than unity. In addition, scattered light may cause problems. Furthermore, the reflectivity depends on the laser polarization relative to the plane of incidence. It is therefore difficult to maintain constant laser power and polarization when the rotation of the laser beam around the scattering center or changes of the angle of incidence with respect to the molecular beam axis are required. Finally, a beam transmission line involving free propagating laser light and reflective surfaces may easily conflict with reasonable safety regulations.

Optical fibers guide light by total reflection in their core, which is surrounded by a cladding and a protective cover. The index of refraction is largest at the fiber axis. A step-index fiber is characterized by a difference in the index of refraction of the core relative to the cladding by a decrement of the order of 0.5%. A graded-index fiber exhibits a continuous variation of the refractive index according to

\[
n^2(r) = n_0^2[1 - 2\Delta f(r)]
\]  

(9.173)

where \( n_0 \) is the refractive index at the axis. The index variation inside the core of radius \( a \) is given by \( f(r) = (r/a)^\alpha \), with \( \alpha \approx 2 \) being a typical value (see, e.g., Midwinter 1979). For \( r > a \), \( f(r) = 1 \) is valid.

The use of optical fibers for coupling lasers to a given experiment is an elegant solution to most of the problems mentioned here. Optical fiber technology has been implemented successfully in several molecular beam research laboratories for many years (Bergmann, Engelhardt, Hefter, Hering, and Witt 1978; Bergmann, Engelhardt, Hefter, and Witt 1978). Some years ago, widespread use of this technique was severely hindered by
limited availability of suitable fibers. Today, the variety of commercially available fibers and the number of suppliers is increasing rapidly. Large-core fibers for high-power transmission, standard multimode fibers for telecommunications, and polarization preserving single-mode fibers are available. Special fibers of crystalline structure that will be usable in the infrared (IR) beyond 1.5 μm are also under development (see, e.g., Gentile et al. 1979).

Which type of fiber and which optical setup for the coupling of the laser light into the fiber is preferred depends on the particular experimental requirements. Many articles and textbooks dealing with the propagation of light through optical fibers have appeared in recent years (see, e.g., Midwinter 1979). Most of them discuss problems related to optical communications that are of peripheral interest in the context of this chapter. The following discussion is limited to a few aspects that are of relevance to molecular beam experiments.

9.2.2.2 Some Key Features of Fiber Transmission Lines. The type of fibers to be used and the necessary efforts in aligning the input and output coupling elements depend on the desired characteristics of the laser beam involved. The beam quality of most pulsed lasers is relatively poor, and the minimum spot size after focusing is relatively large. Thus, larger core fibers (0.5 to 1.5 mm) are appropriate. It is best to avoid tight focusing, anyway to prevent material damage caused by local high-power density (Van Stryland, Soileau, Smirl, and Williams 1981). Despite their large diameter, such fibers are sufficiently flexible. They tolerate bending radii of the order of 10 cm and are easy to handle. Imaging of the laser beam into the core of the fiber is trivial. Net maximum transmission through the fiber without antireflective coating or index matching measures is of the order of 90%. The spectral purity of the laser beam at the fiber exit, however, requires special attention. A significant percentage of the output power may be shifted in frequency because of nonlinear processes such as Raman or Brillouin scattering and self-phase modulation in the fiber core (see, e.g., Hill, Kawasaki, Johnson, and Fujii 1979; and Lin, Nelson, Marshall, and Theobald 1979).

Medium-size-core multimode fibers (50–150-μm core diameter) are convenient for the transmission of CW laser beams in the visible or near infrared in the power range of up to about 10 W. Net transmission of the order of 80% is attainable with only moderate effort in aligning the fiber and coupling optics. The light leaving the fiber, however, has lost the original quality of the spatial intensity distribution (polarization and gaussian profile). This occurs because the light propagates in many modes of the fiber. Each mode is characterized by a specific speed of propagation and a specific spatial intensity distribution (Midwinter 1979). The superposition of the light traveling along different modes leads to a complicated irregular spatial intensity variation (speckle pattern) that changes with minute displacements or bending of the fiber or with very small changes in temperature. Thus, although the net transmission of the fiber remains constant, the local intensity and polarization in a given spot of the beam may change dramatically. Obviously a change in local intensity is intolerable when multiphoton processes are involved in the detection process.

For single-photon laser-induced fluorescence detections, large
local intensity fluctuations cause no severe problems as long as the number of photons along a given trajectory across the laser beam does not change significantly when averaged over the data collection period. This is true, in particular, if detection occurs in the limit of weak excitation \( (E < 1) \).

A given state of polarization can be restored by introducing polarizers. This is achieved, however, only at the expense of intolerably large intensity fluctuations unless an elaborate feedback loop for intensity stabilization is installed.

Single-mode fibers with a core diameter of the order of about 5 \( \mu m \) must be used if the experiment requires precise control of the spatial intensity distribution across the laser beam or diffraction-limited focusing. Such fibers have proven to be useful (Heffter et al. 1986) up to a laser power of the order of 1 W, which is typical for continuously tunable dye lasers. The effort in aligning the coupling optics increases significantly compared with multimode fibers. Net transmissions of the order of 50\% are typically achieved. The necessary tight focusing of the laser beam precludes the use of single-mode fibers in connection with high-power lasers, unless the fiber is specifically meant to be used to generate coherent radiation shifted in frequency by nonlinear processes in the fiber material. Again, laser polarization is not preserved in standard single-mode fibers.

Molecular beam experiments involving the preparation and detection of molecular alignment (see section 9.1.5) require a high degree of laser polarization. If optical fibers are to be used for such experiments, the application of single-mode polarization preserving fiber (see, e.g., Rashleigh 1983) is mandatory. A single-mode fiber with perfect cylindrical symmetry of the optical properties guides light in two modes of identical spatial intensity profile but with orthogonal polarization. The propagation constant of these modes is the same, and coupling between them will be strong. Minor distortion of the fiber (tension, bending, temperature variations) changes the coupling and causes the polarization of the laser light leaving the fiber to change. Intentional distortion of the optical symmetry of the fiber core in the manufacturing process removes the degeneracy of the two modes and strongly reduces the coupling between them. Efficient coupling of laser light into such fibers requires not only the adaptation of the focus diameter to the diameter and numerical aperture of the core but also control of the direction of the laser polarization, \( \hat{z} \), for optimum excitation of the preferred mode of the fiber. With careful alignment, the polarization of the light leaving the fiber typically exceeds \( I_{\parallel}/I_{\perp} = 100:1 \).

9.2.2.3 Mounting and Alignment of Fibers. Coupling of laser light into the core of optical fibers requires a stable and finely adjustable mount. Since not every suitable fiber is available as a mounted cable, the fiber must be mechanically protected as well. Although the mechanical strength of commercially available fibers has increased significantly recently, insertion of the fiber in a flexible Teflon hose (outer diameter \( \approx 1.5 \) mm, inner diameter \( \approx 0.5 \) mm) has proven to be advisable. The small inner diameter of the hose together with the relatively large thickness of the walls prevents the development of kinks that would damage the fiber. The fiber is easily inserted by simple mechanical pushing for a length of up to 10 m, but for extended lengths, the friction is too
great. In these cases, the following procedure has been found to be suitable. The hose is straightened and one end is attached to a small vacuum pump (Fig. 9.23). When the pump is operating, the fiber is pulled through the hose. It is helpful to use a powdered lubricant (talcum) and to control and support the process manually.

Preparation of high-quality end faces of the fiber is surprisingly easy. Cutting machines involving diamond wedges have been described (Gloge 1976) and are commercially available. In most cases, however, burning away the fiber's protective plastic coating and breaking the fiber manually by imposing a sharp bend will yield a clean end surface perpendicular to the fiber axis for fibers with a diameter of up to 200 \(\mu\)m. Larger fibers must be polished. Optical inspection under a microscope is advised. Determining the transmission of the fiber and observing the exiting laser light are usually adequate for judging the quality of the surface. The axis of the light cone should be parallel to the axis of the fiber near its end, and the intensity profile should be circularly symmetrical (except for the speckle pattern in the case of multimode fibers). While fiber cables can be purchased with mounted connectors, homemade fiber cables can be mounted as shown in Fig. 9.24. The hose is inserted into part A and held in place with small screws. The fiber is attached to this part by a droplet of wax. Part A slides into part B, which holds the front piece (part C). The latter has a concentric hole at the tip of the cone, the diameter of which should match as closely as possible the outer diameter of the fiber. A slit in the front section of part B provides some flexibility for the diameter of this piece. It firmly holds the endpiece (part C) when part D or E is mounted and screw F is tightened. The position of part A inside part B is then adjusted until the fiber extends no more than a fraction of a millimeter beyond the endpiece, part C. Thermal contact between the fiber and surrounding metal can be improved with a silver paste. Applying this paste turned out to be useful for input powers exceeding 0.5 W. It minimizes the thermal load on the fiber and reduces the amplitude of microscopic movements that would lead to modulation of the transmission. Epoxy should not be used, because the high intensity in the laser focus will easily evaporate some material.
in the initial alignment procedure, and material deposit on the
front surface of the fiber could occur. At the output side, part E is
used instead of part D. The distance of the lens with \( f = 10 \text{ mm} \)
focal length from the fiber can be adjusted to focus the diverging
light beam exiting the fiber. The mounting technique described
here renders the fiber a versatile plug-in-type connection between
the laser and the apparatus.

Efficient coupling of laser light into the fiber requires the careful
matching of the divergence and the size of the focus of the laser
beam, \( \omega_0 \), to the numerical aperture, \( N_a \), and the core size, \( \omega_c \), of
the fiber. The numerical aperture specifies the range, \( \theta_{NA} \), of
angles, relative to the fiber axis, within which the light rays are
guided by total internal reflection. Both \( \omega_0 \) and the divergence
\( \tan \theta_0 \) of the laser beam should be smaller than \( \omega_c \) and
\( N_a = \sin \theta_{NA} \), respectively. Using equation (9.161) and \( N_a = \tan \theta_{NA} \)
leads to

\[
\frac{\lambda}{\pi N_a} \leq \frac{\lambda f^*}{\pi \omega_c} \leq \eta \omega_c
\]  
(9.174)

where \( \tan \theta_0 = \omega_0 / f^* \) has been used to correlate the waist size,
\( \omega_0 \), and the size \( \omega_c \) of the nearly parallel laser beam at the
coupling lens of focal length \( f_c = f^* \). For optimum coupling into a
graded index fiber, \( \eta \) should be of the order of 0.8. It may be
difficult, especially for single-mode fibers, to satisfy the conditions
specified by equation (9.174) with a lens from a given set. Thus, a
system of two lenses with an effective focal length \( f^* \), may be
required. It is easy to show that

\[
f^* = \frac{f_c f_e}{\Delta L - (f_c + f_e)}
\]  
(9.175)

for two lenses at a distance \( \Delta L \), with \( f_c \) and \( f_e \) being the focal
length of the lens facing the laser and fiber, respectively. The
waist, \( \omega_0 \), is then found near the distance

\[
L_c = \frac{f_c(\Delta L - f_e)}{\Delta L - (f_c + f_e)}
\]  
(9.176)

of the coupling lens.

Fine adjustment of the focusing device is required, to align the
laser beam and the fiber. A setup is shown schematically in Fig.
9.25. The distance between the fiber and the lens \( (z_i) \), as well as the
positions perpendicular to the axis of the lens \( (x_i \text{ or } y_i) \), are
adjustable. Standard micrometer screws are adequate for multi-
mode fibers with a core diameter exceeding 30 \( \mu \text{m} \). Coupling into
a single-mode fiber requires additional fine tuning, because of the
very small core diameter of these fibers. Fine tuning can be
achieved by small displacements of the axis of the fiber and lens
relative to the axis of the laser beam. This can be performed by
either displacing the entire assembly of fiber and lens perpendicu-
larly to the laser beam \( (X_2 \text{ and } Y_2) \) or, alternatively, displacing the
laser beam by inserting one or two plane parallel glass plates that
are rotatable around two perpendicular axes. Parallel displace-
ment of the laser beam by \( \Delta s \), relative to the optical axis of the
lens of focal length \( f \), results in displacement of the laser focus by
\( \Delta s' = \Delta s f / L \), with \( L \gg f \). \( L \) is the distance of the waist of the
laser beam from the lens. Alternatively, a lens of appropriate focal
length can be used instead of the plate. Adjustment of the lens in
the \( X_2 \) and \( Y_2 \) direction causes a small displacement of the focus...
relative to the center of the fiber. Compact devices for mounting and accurate alignment of monomode fibers relative to the focus of a laser beam are now becoming commercially available.

9.2.2.4 Double Focus Setup for Two-Photon Excitation. Recently resonant two-photon excitation or ionization schemes have become an important analytical tool (see section 9.3.1). This produces the problem for CW lasers of accurate superposition of two tightly focused laser beams (see Bergmann and Gottwald 1981; section 9.2.3.3). If optical fibers can be used, the following compact design (see Fig. 9.26) provides an elegant solution. Two separate fibers are combined in a single hose and are mounted in parallel in the endpiece (part C, Fig. 9.24). The axes of the fibers are $\Delta s$ apart ($\Delta s = 100 \mu m$). The outputs of both fibers are transformed into a nearly parallel beam of light (Fig. 9.26b). In the configuration depicted in the figure, the separation $\Delta s'$ of the cylindrical foci of the two laser beams is $\Delta s' = \Delta s f_e/f_s$, where $f_e$ and $f_s$ are the focal length of the cylindrical lens and spherical lens, respectively. With $f_e = f_s$, $\Delta s'$ is also of the order of 100 $\mu m$. When the fibers are rotated through an angle $\varphi_F$ without rotation of the cylindrical lens, a vertical and horizontal displacement of the cylindrical foci results. Because the vertical extension of the foci will be of the order of 1 to 2 mm, the net effect is a horizontal displacement of the foci relative to each other. For $\varphi_F = 180^\circ$, the relative displacement is $\Delta s'$. Thus, the tuning sensitivity is of the order of 1 $\mu m$ per degree of rotation.

9.2.2.5 Monitoring Transmitted Laser Intensity. It is necessary in most experiments to measure or monitor the laser power transmitted through the fiber inside the vacuum chamber. Placing

![Figure 9.25 Schematic of the alignment of the laser beam, lens, and fiber. For efficient and stable coupling of laser light into the core of the fiber, the lens and the fiber must be adjustable in the $x_1$, $y_1$, and $z_1$ directions relative to each other. Coupling into a single-mode fiber requires additional fine tuning by displacing the axis of the laser beam relative to the axis of the lens and fiber. This can be achieved by either displacing the optical setup as a whole in the $X_2$, $Y_2$ direction or by displacing the laser beam through the rotation of a sufficiently thick parallel plate.](image-url)
a partially transmitting glass plate, a mirror, or a photodiode directly in the laser beam, invariably leads to an undesirable increase of scattered light in the detector. The simple setup shown in Fig. 9.27 provides a convenient solution. When the curvature of the fiber exceeds a critical value, a small fraction of light is lost from the core. The light leaving the fiber can be detected with a closely attached photodiode. The diode signal gives the laser power, provided the device has been calibrated by measuring the transmitted power before the fiber is located inside the vacuum chamber. This setup is also suitable for optimizing the coupling of the laser light into the fiber if the intensity and spatial profile of the transmitted light cannot be measured directly and coarse alignment has already been done. The diode signal will be relatively large when a fraction of the light is coupled into the cladding. It is minimal for optimum coupling into the core.

9.2.2.6 Fiber Bundles. Single-optical fibers are inadequate for collecting laser-induced fluorescence because of their small surface area. The useful surface area of a fiber bundle is typically 70% of the geometric surface. Such bundles are very convenient for detection purposes, because they provide a flexible link between the photon collection device and a photomultiplier. The latter can be located outside the vacuum chamber. Fiber bundles are commercially available with a large variety of dimensions. Circular bundles are most commonly used. Since the fluorescence emerges quite often from a cylindrical volume rather than from a circular one, rectangular bundles may be advantageous. Finally, a bundle with a circular cross section at one end and a long, narrow cross section at the other end provides a convenient interface between the light-collecting optics and the entrance slit of a monochromator.

For standard vacuum requirements, vacuum feedthroughs are also commercially available, albeit not as standard items. In the feedthrough section the flexible protective cover of the bundle is replaced by a short rigid tube and the volume between the fibers is filled with epoxy. For ultrahigh vacuum environments, epoxy-free fiber bundles must be used and the bundle should end at the vacuum side of an exit window with the photomultiplier (or another bundle) attached at the other side.

9.2.3 Collection of Laser-Induced Fluorescence

9.2.3.1 High-Speed Optics. To collect the largest possible fraction of emitted photons at the lowest possible level of background light is normally the goal. If analysis of the polarization, $\hat{P}$, of the fluorescence is required, and since $\hat{P}$ changes with the direction of photon emission relative to the laser polarization, high-speed collection optics is inappropriate for the measurement of fluorescence polarization. Correction factors to account for the averaging over a small solid angle are given by Zinsli (1978). The optimum compromise between optics speed and measures to suppress scattered light is determined by the given experimental problem.

A setup for high-speed optical detection is shown in Fig. 9.28. Following the suggestion of Shimizu and Shimizu (1983), two cylindrical aluminum blocks with polished and coated spherical surfaces of different radii, $R$, of curvature are fastened to a

---

**Figure 9.26** (a) Combination of two fibers that carry light from different laser sources into a single hose. (b) Setup for accurate superposition of the lightly focused light from two individual fibers. Rotation of the endpiece (E) with the two fibers through $\varphi_F$ results essentially in a displacement of the foci of the light from the two fibers relative to each other. (c) Setup for the coupling of light from two different sources into a single fiber, using a dichroic mirror.

---

**Figure 9.27** A small fraction of light leaves the fiber that is bent with a radius of $r \approx 5$ cm. It is monitored with a large-area photodiode. With proper calibration, this setup gives an accurate measure of laser intensity exiting the fiber.
support block. The left-hand mirror has a radius $R = 25\, \text{mm}$ and reflects the fluorescence light back into the volume, where the laser beam and the collimated molecular beam intersect. The other mirror has a radius of $R = 18\, \text{mm}$ near the detector axis. To correct for imaging errors of a spherical surface, the outer segment has $R = 19\, \text{mm}$. This mirror reflects the light onto the surface of a fiber bundle that is inserted at the center of the opposite mirror. Assuming an angle of acceptance of $60^\circ$ for the fiber bundle, photons from about 80% of the full solid angle are collected (see also Bergmann et al. 1979). An alternative arrangement uses a reflective surface of ellipsoidal shape with the source of the fluorescence near one focal point and the detector or surface of the fiber bundle at the other focal point.

9.2.3.2 Suppression of Scattered Light. The intensity of scattered light is often the factor limiting the sensitivity of a given experimental setup for collection of laser-induced fluorescence. Scattered light increases linearly with the laser intensity, whereas the laser-induced fluorescence will eventually saturate. Optimization of the signal-to-noise ratio may require reduction in laser intensity. This is particularly necessary if the signals caused by scattered light and by laser-induced fluorescence are of comparable magnitude.

Several measures for reducing the level of scattered light without sacrificing signal can be applied. Scattered light arising from the entrance and exit windows of the laser beam can be suppressed by a series of sharp-edged diaphragms. Since light striking the edges of the diaphragms contributes to the scattered light, the diameter of the first one should exceed the $e^{-2}$ radius of the laser beam. For the detection of fluorescence induced by pulsed lasers, a stack of 5 to 10 apertures over the path length of up to 1 m has proven to be appropriate (Fig. 9.29). Such baffles should be used for both the entrance and exit windows. If the direction of linear polarization of the laser must be changed, or if circular laser polarization is used, the entrance window must be perpendicular to the laser beam axis, to prevent modulation of the incident laser power. The laser should not impinge perpendicularly to glass surface of the exit window, however, because the reflected beam will increase the level of scattered light significantly. An angle of the order of $45^\circ$ is convenient for trapping the photon of the reflected laser beam in a beam dump (see Fig. 9.29).

Coating all the surfaces in the vicinity of the axis of the optical detection system with optical flat black paint is another efficient measure for reducing scattered light. It is important, however, to verify that the paint is nonfluorescent. This is especially true if cutoff filters are used to separate the scattered laser light from the molecular fluorescence, the wavelength of which is red shifted with respect to the laser. Red-shifted fluorescence from the surface coating will also leak through the filters.

When most of the fluorescence occurs at, or near, the laser wavelength, cutoff filters cannot be used and spatial filtering must be applied. The standard setup is shown in Fig. 9.30a. A high-speed optical lens system collects light from a large solid angle and focuses the fluorescence through a small diaphragm onto the detector. Light collected by the lens system that originates from other regions will be rejected by the mask in front.
of the detector. Efficient spatial filtering requires careful positioning of the pinhole. A retroreflector (see also Fig. 9.28) can be used to enhance the signal level. To minimize the scattered light intensity, the retroreflector can be replaced by a light trap (see Fig. 9.29). A modification of this setup, which allows one to conveniently vary the location from which light is collected, is shown in Fig. 9.30b (see also Smalley, Levy, and Wharton 1976). The first high-speed lens forms an enlarged image of the spatial region to be investigated. A field lens refocuses the diverging light by imaging the collecting lens onto the lens in front of the detector. A mask with a small hole in the plane of the image next to the field lens defines the spatial region from which fluorescence may reach the detector.

9.2.3.3 An Effect of Optical Pumping. Spatial filtering for the reduction of scattered light is particularly important when the excitation probability approaches the limit of saturation ($E \rightarrow 1$). In this case, however, an effect of optical pumping may nullify the advantage of spatial filtering when the excitation occurs with a CW laser or with a laser pulse of length $\Delta t_L$ that is longer than the transit time, $\Delta t_L$, of the molecules through the laser beam. Figure 9.31 shows the fluorescence intensity and the ion signal resulting from two-step photoionization of Na$_2$ as the laser frequency is tuned across the resonance of a molecular transition. Photons are collected from an area much larger than the laser diameter. Because of the small cross section for photoionization, the second step is not saturated and the number of ions produced in a small volume $dV$ is proportional to the laser intensity in this volume. Thus, ions are expected to originate predominantly from the axis of the laser beam.

With increasing laser power, the photon signal, as a function of laser frequency, broadens while the ion signal develops a

Figure 9.29 Scattered light intensity can be significantly reduced with laser light baffles near the entrance and exit windows, using light traps on the axis of the optical detection system and for the beam reflected from the exit window and by spatial filtering of the collected light.

Figure 9.30 Reduction of scattered laser light reaching the detector by spatial filtering. (a) A high-speed lens system collects light and focuses it onto a small hole in front of the detector. A retroreflector can be used to increase the fraction of collected light. Alternatively, a light trap (Wood's horn) can be installed to further reduce the amount of scattered light. (b) Spatially filtered light can be collected from various locations with a stationary lens system, if a movable mask is introduced at the location of the enlarged image of the source. A field lens refocuses the light, essentially by imaging the surface of the high-speed lenses onto each other.
pronounced dip (see Bergmann and Gottwald 1981). A similar dip would be observed in the photon signal if spatial filtering were used to limit the detection to fluorescence originating from an area near the laser axis. The reason for this becomes obvious from Fig. 9.32, which gives the 50% intensity contour of the laser as well as the 90, 50, and 10% contours of the density of molecules in the excited state. These results are obtained from the solution of the rate equations (see section 9.1.2.4) for individual flight paths through the laser beam. For low excitation probability, the density contours are nearly concentric to the laser beam axis. With increasing excitation probability, more molecules are excited in the wings of the profile. If the flight path of the molecules in the excited state is small compared with the laser diameter, the ground state population is depleted because spontaneous decay occurs predominantly to levels other than the original one. Thus, fewer molecules that can contribute to the ion signal (or to the fluorescence, in the case of restrictive spatial filtering) reach the center of the laser beam.

Restrictive spatial filtering should be avoided particularly if a detector in a magic angle arrangement is used (see Section 9.1.1.3), to ensure a detection efficiency independent of the quantum number $m$. Since the excitation probability varies with $m$, the extent to which the effect of optical pumping reduces the detection efficiency, $D(i)$, depends on $m$. Thus, optical pumping in connection with spatial filtering may reintroduce an $m$ dependence of $D(i)$.

9.2.3.4 Increasing the Duty Cycle in Pulsed Laser Excitation. A drawback of particle detection with pulsed lasers is the low duty cycle. With pulsed lasers, excitation often occurs near the limit of saturation. In that case, the photons are used more efficiently if the laser beam is spatially expanded with cylindrical lenses parallel to the molecular beam axis, provided photons can be collected from the enlarged area. If the repetition rate of the laser pulse is of the order of $(\Delta \tau)^{-1}$, where $\Delta \tau$ is the transit time of the particle through the laser beam, the effective duty cycle may approach unity. This can be achieved, however, only for high repetition rate lasers.

9.2.4 Special Problems Related to the Detection of Fluorescence with Photomultipliers

When relating the observed signals to level populations, it must be established whether the flux, $Z$, of photons (photons/second) or the intensity, $I$, of fluorescence (watts) is measured. The photon count rate is proportional to $\sum_{i} \frac{\omega_{\text{int}} \cdot T_{\text{r}} \cdot Q_{\text{r}}}{Q_{\text{m}}}$ [see equation (9.106)].

Photomultipliers are widely used because of their high sensitivity and very large dynamic range. They measure $Z$ rather than $I$, independent of whether they operate in the photon counting mode or the current mode. In both cases, a photon of energy $h \nu_{\text{ph}}$ produces a photoelectron with the probability $Q_{\text{m}}$, which is converted to a pulse of $10^{6}$ electrons at the anode of the photomultiplier independent of $\omega_{\text{ph}}$. Typically, $\beta$ ranges from 6 to 8.

Signal detection in the photon counting mode is limited to count rates significantly smaller than $\Delta \tau^{-1}$, where $\Delta \tau$ is the width of the electron pulse arriving at the anode. With $\Delta \tau = 10^{-3}$ s, the count

Figure 9.31. Simultaneously measured fluorescence and resonant two-photon ion signal of N$_2$. The detection optics collects light from an area much larger than the diameter of the laser beam. Ions are produced primarily in the center of the beams. With increasing laser intensity, a dip related to optical pumping develops in the ion signal. A similar dip would occur in the fluorescence signal if collection of light were limited to a small area near the axis of laser beams. [Reproduced from Bergmann and Gottwald (1981).]
rate should not exceed a few $10^9 \text{s}^{-1}$. For larger pulse rates, pileup corrections must be applied. Such corrections account for the fact that two photons may initiate one photoelectron each within the time resolution of the multiplier or the counting electronics. These two photons will be registered only as a single event. Pileup corrections are not necessary if the current is measured. Nevertheless, too large values of amplified photoelectron current should be avoided, to prevent a decrease in net amplification.

Laser-induced fluorescence from pulsed lasers should be detected in the photon counting mode only if the probability of detecting a photon in $\Delta t_p$ is smaller than unity. The pulse length of excimer-pumped dye lasers is of the order of $\Delta t_p$, and the probability to detect a photon per laser pulse must be small. Otherwise, the detection characteristic becomes highly nonlinear. If, for instance, one scattered laser photon per pulse is detected on the average, any increase in the signal level, such as when the laser frequency is tuned across a molecular transition, remains undetected. Again, these problems are not encountered if the photoelectron current is measured.

9.3 Detection by Photoionization

9.3.1 Brief Survey of Ionization Pathways

With the advent of powerful lasers, photoionization has become a universal and efficient detection scheme for atoms and molecules. It is an intrinsically sensitive technique because ions can be collected and detected with high efficiency. When combined with mass selective detection, this method is particularly attractive for the spectroscopy and detection of molecules in the presence of other species that have congested absorption spectra in the same spectral region (see, e.g., Kappes, Marti, Radi, Schär, and Schumacher 1984). An early example for detection of particles in a beam experiment by photoionization is the work of Feldman, Lengel, and Zare (1977). They detected the BaCl product from the barium + HCl reaction. Numerous applications in spectroscopy and collision dynamics have been reported recently, only a few examples are discussed here.

A straightforward approach is the one-photon ionization directly into the ionization continuum (see, e.g., Herrmann, Schumacher, and Wöste 1978; Hepburn, Klimk, Liu, MacDonald, Northrup, and Polanyi 1981; Peterson, Dao, and Castileman 1983; Broyer, Chevaleyre, Delacretaz, Fayet, and Wöste 1985). One-photon ionization requires relatively high-energy photons. Only a few particles with low ionization potential, such as alkali atoms, molecules, and clusters, can be ionized with one photon from readily available lasers or conventional light sources. Furthermore, the cross section for single-photon ionization, from the ground state directly into the ionization continuum, is relatively small and the process is not selective with respect to individual rotational–vibrational levels of a molecule. More sophisticated multiphoton processes have been applied to overcome these constraints. For detection purposes, they involve enhancement of the ionization efficiency by a resonant intermediate level.

Two-photon ionization by means of an intermediate electronic state, called a “$1+1$” process (see, e.g., Esherick and Owyong 1983; Meier, Rottke, Zacharias, and Welge 1985; Jacobs, Madix, and Zare 1986) or excitation to an autoionizing Rydberg level.
(see, e.g., Hermann, Leutwyler, Schumacher, and Wöste 1977; Leutwyler, Hermann, Wöste, and Schumacher 1980; Eisel, Demtröder, Müller, and Botschwa 1983), are well-established techniques. The framework for the reduction of "1+1" resonantly enhanced ionization spectra to population and alignment factors has been worked out (Jacobs and Zare 1986; see later). More sophisticated schemes involve multiphoton transitions to a resonant intermediate state out of which the molecule is photoionized. This approach avoids the use of photons in the vacuum ultraviolet (VUV) spectral region. Molecules with high-lying electronic states can be excited to an intermediate level by a two-photon process (see, e.g., Kligler, Bokor, and Rhodes 1980; Marinero, Rettner, and Zare 1982; Conaway, Morrison, and Zare 1985; Arepalli, Presser, Robie, and Gordon 1985) or by three-photon excitation processes (Pratt, Dehmer, and Dehmer 1983) followed by a one-photon ionization. These are "2+1" and "3+1" processes, respectively. Other multiphoton ionization pathways have also been demonstrated. Examples are two-photon excitation of an intermediate level of NO (Esherick and Anderson 1980) or N₂ (Carleton, Welge, and Leone 1985) followed by a two-photon ionization ("2+2" processes). Detection of fluorine atoms by means of a "3+2" process has recently been reported by Bischel and Jusinski (1985). Even double enhancement in the photoionization of NO by means of a "2+1+1" process (two-photon excitation of the A superscript 2Σ state with subsequent excitation to a Rydberg level, followed by transition to the ionization continuum) has been observed (Steimle and Liou 1983).

9.3.2 Qualitative Features of Photoionization Detection
The detection scheme based on resonantly enhanced two-photon ionization has several striking advantages but is also plagued by severe problems, when quantitative analysis is required. The ionization rate depends critically on the temporal and spatial intensity profile of the laser. Detection of the ions rather than electrons is preferable because the former are less susceptible to stray magnetic fields. Detection and energy analysis of the photoelectrons, however, is, needed to determine the internal energy of the ion (Pratt, Dehmer, and Dehmer 1984a,b; Conaway, Morrison, and Zare 1985).

Once the ions are created, they are easily detected and even mass analyzed. A simple electrostatic extraction system and a charged particle detector separated by a flight path is all that is needed. Such a device used in conjunction with a pulsed laser is a time-of-flight mass spectrometer. Unlike for photon detection, the signal level does not suffer from inefficient collection optics and low quantum efficiencies of photomultipliers. Mass selective detection also reduces or even eliminates interference from ions related to the background gas. Furthermore, unlike for photomultipliers, the dark counts of charged particle detectors are almost negligible. Because of these features, photoionization involving pulsed lasers is a very successful technique for detecting particles or monitoring the flux of molecules in a given quantum state.

Under very fortunate circumstances, efficient photoionization with only a few milliwatts of CW laser power is possible. The two-step photoionization of alkali dimers by means of a low-lying electronic state and an autoionizing Rydberg level is an example (Bergmann and Gottwald 1981).
The quantitative application of the photoionization technique is more difficult because the relationship between the ratios of ion signals and the ratio of populations is substantially more complex than in laser-induced fluorescence.

9.3.3 Quantitative Analysis
The most promising and experimentally least complex approach is the "1 + 1" resonantly enhanced photoionization with both photons coming from the same laser. The cross section for the resonant excitation step is typically several orders of magnitude larger than the cross section for ionization out of the excited state (Fig. 9.33). The smallness of the latter requires a powerful laser for efficient ionization, with the consequence that the resonant excitation occurs in the regime of saturation. This mismatch of cross sections causes a complex dependence of the ion signal on laser power and level population as well as on molecular alignment. Under typical experimental conditions, the power dependence of the ion signal is neither linear nor quadratic. It is also different for the different branches of spectroscopic transitions. Normalization of the signal with respect to laser power is therefore an involved procedure. Furthermore, saturation changes the polarization of the intermediate level, which in turn affects the rate of ionization with polarization laser light.

Recently, Jacobs and Zare (1986) presented the theoretical framework for the quantitative analysis of "1 + 1" photoionization spectra with a single laser source. Jacobs, Madix, and Zare (1986) demonstrate the feasibility of this scheme by applying it to the detection of NO (see Fig. 9.34). Their procedure is briefly described in the following. They solve the rate equations for population transfer within the appropriate level system (Fig. 9.33) involving resonant absorption, spontaneous and stimulated emission, and ionization. Quantum mechanical expressions for the rate constants for radiative transitions are used for individual \((j, m) \rightarrow (j', m')\) transitions, assuming linear laser polarization. Coupling to neighboring \(m\) levels of level 0 by spontaneous emission from level 1 is neglected. The ion signal is obtained by summation over all \(m\) levels.

The solution of the rate equation yields (Jacobs and Zare 1986) for the number of ions

\[
N_i(\Delta t_i) = N_i(0) F_{ir}(k_0, k_2, I\Delta t_i) \tag{9.177a}
\]

with

\[
F_{ir}(k_{01}, k_{12}, I\Delta t_i) = 1 - (2B)^{-1} \left[ (A + B) \exp \left( -\frac{1}{2} (A - B) I\Delta t_i \right) - (A - B) \exp \left( -\frac{1}{2} (A + B) I\Delta t_i \right) \right] \tag{9.177b}
\]

\[
A = 2k_{01} + k_{12} \quad \text{and} \quad B = (4k_{01}^2 + k_{12}^2)^{1/2}
\]

The duration of the laser pulse of intensity \(I\) is \(\Delta t_i\). Jacobs et al. (1986) show by numerical analysis that the exact form of the pulse shape is of minor importance, provided the electronic lifetime, \(\tau\), of the resonant level is much longer than the pulse duration. What matters is the time-integrated pulse intensity (see, however, section 9.3.4). Thus, for simplicity a rectangular pulse of intensity \(I\) and duration \(\Delta t_i\) can be assumed (see also section 9.1.2 and Fig. 9.9). Derivation of equation (9.177) is based on the assumption
that the laser power density is constant over the ionization volume. Thus tight focusing of the laser beam is excluded. Equation (9.177) shows the nonlinear dependence of the ion signal on the integrated laser intensity $I$.

The rate constant $k_{01}$ varies with the overlap of laser bandwidth and molecular absorption frequency [see equations (9.28) through (9.32)], whereas the variation of the rate constant $k_{12}$ for the bound-to-continuum transition is expected to be small. This eliminates ionization pathways involving autoionizing Rydberg levels. Such resonances will be encountered only accidentally in “1 + 1” processes using one laser. Because of the relatively small ionization cross section, $k_{12}I \Delta t_i \ll 1$ will be valid and $F_{sat}$ will be proportional to $k_{12}$. Thus, $k_{12}$ must be determined only once for a given system.

The rate constant for the resonant transition

$$k_{01}(m) = 3C_{01-S_{ho}} \frac{j_1}{j_0} \left( \begin{array}{c} j_1 \\ m \\ 0 \\ -m \end{array} \right) \right)^2$$

is $m$ dependent. $C_{01}$ is of the order of $c^2/(8\pi v^2 \Delta \nu_{N})$ but also depends on the overlap of laser bandwidth $\Delta \nu_{V}$ and molecular transition line width $\Delta \nu_{N}$.

The $m$-dependent rate constant for photoionization by means of a $^1 \Sigma$ intermediate state can be written as

$$k_{12}(m) = 3(2j_1 + 1) \frac{\sigma}{\hbar \nu} \sum_j (2j_2 + 1) \left( \begin{array}{c} j_2 \\ m \\ 0 \\ -m \end{array} \right) G(\Gamma)$$

with

$$G(\Gamma) = \Gamma \left( \begin{array}{c} j_2 \\ 0 \\ -j_1 \end{array} \right)^2 \left( \begin{array}{c} 1 \\ j_1 \end{array} \right)^2 \left( \begin{array}{c} 1 \\ 1 \\ -1 \end{array} \right)$$

Expressions for generalized intermediate states are given by Jacobs and Zare (1986). The ionization cross section is $\sigma$, while $m$ and $Q$ are the projections of the total angular momentum on the laser polarization and internuclear axis, respectively. Because the continua of more than one electronic transition may be involved, the fraction $\Gamma$ of parallel and perpendicular $(1 - \Gamma)$ character must be determined. The terms parallel and perpendicular refer to the direction of the transition dipole moment with respect to the internuclear axis (see Chapter 12, Fig. 12.14). The ion signal is the sum of equation (9.177) for each $m$ level. In practice, the pulse-to-pulse fluctuations of the laser power at a given laser frequency are sufficiently large to collect enough data (ion count rate and laser power) for a nonlinear least-squares fit, yielding the parameters $N$ and $k_{01}$ (averaged over $m$) at each wavelength. Once the functional form of $F_{sat}$ [equation (9.177)] is established, the ion signal can be scaled to any given laser power. A fit procedure to determine $\Gamma$ experimentally is described by Jacobs et al. (1986). The population of level $j$ is then obtained from

$$N(j) = \frac{N_{k_2}(j, \Delta t_i) \Sigma_m f(m) F_{sat}(k_{01}(m), k_{12}(m), I \Delta t_i)}{\Sigma_m f(m) F_{sat}(k_{01}(m), k_{12}(m), I \Delta t_i)}$$

where $N_{k_2}(j, \Delta t_i)$ is the raw data, scaled to the same integrated laser intensity. The relative population of level $m$ is $f(m)$. For
isotropic distribution of the molecular ground state, \( f(m) = 1 \) is valid and equation (9.180) can be evaluated. A Boltzmann plot of \( N(j) \) for various \( j \) values (see section 9.1.4.2) finally yields the relevant temperature for the level population or reveals the extent of deviation from a thermal distribution.

Extraction of alignment information (determination of \( f(m) \)) from the measurement of the laser power dependence of the ion count rate for various directions of linear laser polarization is possible but difficult, as Jacobs et al. (1986) explain in more detail.

### 9.3.4 Line Shape Problems

The observation of the preceding section that the time-integrated intensity, \( I \Delta t_L \), rather than details of the temporal variation of the laser pulse, matters in “+1” ionization is not valid for ionization pathways involving resonant levels with an electronic lifetime \( \tau \ll \Delta t_L \). In this case, optical pumping may reduce the ionization efficiency (see section 9.2.3.3). Furthermore, competition between spontaneous decay and ionization renders the spectral profile of the ionization rate, and thus the ionization efficiency, sensitive to the laser intensity or laser pulse shape. This phenomenon has been observed, for instance, by Haberland, Höhne, Osswald, and Broad (1986). They ionize metastable He(2S) atoms in the singlet or triplet manifold in a two-step process with photons of \( \lambda = 501.7 \text{ nm} \) or \( \lambda = 388.9 \text{ nm} \), respectively, through the 3P or 3D level.

Haberland et al. use two different excimer laser-pumped dye lasers (lasers A and B) with a rise time of the pulses of about 2 ns. Using laser A, the ion yield shows a dip for excitation on resonance with the 2S–3P transition as the frequency is tuned (Fig. 9.35a). This dip is not observed when laser B is used (see Fig. 9.35b). The dip is observed again in an experiment with delayed pulses from laser B when the pulse shape is tailored to exhibit a smoothed leading edge. This is done by splitting the laser beam into two components. A pulse with 95% of the total energy excites and ionizes the atoms approximately 7 ns after a precursor pulse with only 5% of the total energy has interacted with the particles (see Fig. 9.35c). The data of Fig. 9.35 show that spontaneous decay of the intermediate level competes with the rate of ionization. On resonance, a population is established in the intermediate level, even at the very beginning of the low fluence pulse. In this case the intensity-dependent rate of ionization is slower than the spontaneous decay rate. A loss of ionization efficiency results. This is not the case off resonance, when the intermediate level is populated at the pulse maximum only. Then, because of the high fluence, the ionization rate exceeds the rate for spontaneous decay. For fast-rising pulses the spontaneous decay rate is too small to reduce the ionization rate. Because only a small fraction of intensity (~1%) in the leading edge is necessary to produce the dip, this smooth rising of the laser A pulse could not be detected with a photodiode. Other structures in the ionization yield, seen in Fig. 9.35b and c, are not yet understood. Haberland, Osswald, and Broad (1986) provide evidence that they are not artifacts.

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![Figure 9.35](image)

**Figure 9.35** Resonantly enhanced two-photon ionization of He(2P) by means of the 2P state, using excimer-pumped dye lasers of 5-ns pulse lengths. Other specifications are (a) home-built Littman-type oscillator, followed by two amplifier stages, given 0.7 GW/cm² and a bandwidth of 0.6 cm⁻¹ (amplified spontaneous emission is not negligible for this laser); (b) commercial laser with 3 GW/cm² and a bandwidth of 0.3 cm⁻¹ (the center dip was also not observed at lower power densities); (c) the same as in b, but a pulse with 95% of the total energy excites and ionizes the atoms approximately 7 ns after a precursor pulse, with only 5% of the energy, has interacted with the particles. The structure in the wings of the profile seems to be real but is not understood at the present time. [Adapted from Haberland et al. (1986).]
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