State Selection by Optical Methods

K. Bergmann

12.1 Introduction and Selection Principles

It was realized in the early days of molecular beam experiments that state-selective collision experiments would significantly deepen our understanding of collision dynamics. Attempts have been made to select atomic $m$ levels (Berkling, Schlier, and Toschek 1962) or aligned rotational levels of molecules (Bennewitz, Kramer, Paul, and Toennies 1964) using inhomogeneous fields for state-selective deflection or focusing. These techniques have been further developed to conduct a number of sophisticated scattering experiments with polar molecules (see Chapters 11 and 25). A limitation of that technique is the restriction to small $(j, m)$ quantum numbers, at least for experiments aiming at high state selectivity (see, e.g., Mosch, Safron, and Toennies 1975). Also, the small acceptance angle of the focusing device reduces the flux of molecules available in the scattering center. As a consequence, mostly integral or small-angle differential cross section measurements have been undertaken so far. In a favorite case, however, a high-resolution differential cross section could be measured (Tsou, Auerbach, and Wharton 1977, 1979). On the other hand, this selection principle is applicable to a class of molecules that is not always easily accessed by optical techniques. Another early attempt to obtain state-selective data is the work of Blythe, Grosser, and Bernstein (1964). They used time-of-flight velocity analysis (see also Chapter 14), a technique also applied by Beck and Förster (1970) and Schepper, Ross, and Beck (1979) and recently developed as a high-resolution technique (see, e.g., Buck, Huisken, Schleichener, and Pauly 1977; Faubel and Toennies 1977; see also Chapter 21). An early attempt to modify the vibrational excitation prior to a collision process in beams is reported by Crim, Chou, and Fisk (1973). They used a triple-beam arrangement to form highly vibrationally excited potassium bromide (KBr) molecules in a reaction of K + Br$_2$ that were subsequently scattered off various target molecules.

State selection by optical methods, the subject of this chapter, has only very recently become a general and versatile tool in molecular beam collision experiments. Work related to state-selective detection (see Chapter 9) and state preparation exclusively for spectroscopic techniques (see Volume 2, Chapters 7 and 8) is excluded here.

The original idea of Kastler (1950) (see also Brosset, Kastler, and Winter 1952) focused on the attempt to align atomic angular
momenta by redistribution of the \( m \)-level population through optical pumping with polarized light. The nonisotropic distribution over \( m \) levels was then used for spectroscopic studies, for example, for the detection of radiofrequency absorption. This paved the way for the development of the optical analog of molecular beam resonance techniques (Rabi, Zacharias, Millman, and Kusch 1938; Ramsey 1956). The first application of these principles involving laser state selection to RF spectroscopy of molecules in a beam seems to be the work of Rosner, Holt, and Gaily (1975) on \( \text{Na}_2 \), followed by the work of Yokozeki and Muenter (1980) on \( \text{I}_2 \) (see also Volume 2, Chapter 2). They used state-selective depletion rather than radiative redistribution of \( m \)-level population to measure nuclear quadrupole moments, for example.

Most of the basic ideas of atomic or molecular state selection by optical means were formulated before or shortly after the advent of the laser (Kastler 1950; Dehmelt and Jefferts 1962; Bersonh and Lin 1969; Zare 1972). Originally most of these were aimed at application in the bulk (Drullinger and Zare 1969, 1973; Bergmann and Demtröder 1972), but no fundamental problems hindered the transfer of these techniques to molecular beams. Widespread application of these techniques, however, had to await the development of more refined spectroscopic techniques (Demtröder 1981) and the availability of dependable CW and pulsed lasers. The first application of lasers for detection of reaction products (Schultz, Cruse, and Zare 1972) and molecular state selection in crossed beams experiments (Bergmann, Engelhardt, Heffer, Hering, and Witt 1978) dates back only about 10 years. Today optical state selection is beginning to mature as a well-established, successful technique. The combined selectivity and sensitivity of laser state selection and detection has revolutionized collision dynamics experiments.

State selection through optical methods is almost exclusively synonymous with laser state selection. The only exception included in this chapter is discussed in section 12.3.3.3. Only laser radiation carries a sufficiently high spectral density for significant manipulation of the thermal population of atomic or molecular levels in a beam. Optical state selection techniques have emerged from methods developed in laser spectroscopy (Demtröder 1981; Shimoda 1976). Spectroscopy, in turn, has benefited significantly from state selection techniques in labeling a small number of transitions in congested spectra. Naturally, laser state selection was first applied to collision experiments in the bulk. Now, most collision experiments in the bulk use state selection and state-selective detection in one way or another. Here, attention is given only to applications in a beam, starting with a brief classification of the various techniques to be discussed in more detail in subsequent sections.

Selective population by a one-photon process is a most straightforward approach. This includes the population of levels in electronically excited states of atoms and molecules by radiation in the visible or ultraviolet spectral region (with too many references to choose from) as well as selective excitation of vibrational levels (see Fig. 12.1a) by infrared radiation (Karn, Estler, and Zare 1978; Disperer, Geis, and Brooks 1979; Hoffmeister, Potthast, and Loesch 1983; Vohralik and Miller 1985). In most cases, the radiation is polarized and the molecular ensemble will be oriented or aligned.
A number of very recent techniques employ state-selective population involving more than one photon. The simplest scheme starts with excitation to a bound electronically excited state. The spontaneous radiation back to the electronic ground state redistributes the molecules among vibrationally excited levels, \( v' \) (Fig. 12.1b). Thus, depending on the variation of the Franck-Condon factors with \( v' \), the population of excited vibrational levels is enhanced (Bergmann, Hefter, and Witt 1980; Gottwald, Mattheus, and Bergmann 1986; Fuchs and Toennies 1986). The molecules can be channelled predominantly into one particular vibrational level by imposing a second laser field that stimulates emission on a given transition (Fig. 12.1c). A rather general scheme for the excitation of the first vibrational level of a molecule uses two powerful pulsed lasers with an appropriate frequency difference to pump molecules with none of the lasers being in resonance with an electronic transition (Fig. 12.1d) (Esherick, Owyoung, and Patterson 1983; King, Haines, Isenor, and Orr 1983; Orr, Haub, and Haines 1984; Chandler and Farrow 1985). Coherent multiphoton pumping schemes, other than those already mentioned (e.g., CARS) have been applied for detection but are less likely to be successful for state selection because of the low density of particles in the beam.

Sequential two-photon absorption can be used to excite high-lying electronic states, including Rydberg levels of atoms (Feneuille and Jacquinot 1981) and molecules (Eisel, Demtroder, Muller, and Botschwina 1983). A particularly intriguing version of this scheme is the formation of vibrationally selected molecular ions (Chupka, Russell, and Refaey 1968; Pratt, Dehmer, and Dehmer 1984a, 1984b; Conaway, Morrison, and Zare 1985), or specific fine-structure states in atomic ions (Siegel, Ganz, Bussert, and Hotop 1983; Kimura 1985). The first excitation step may involve simultaneous absorption of one or more photons. The combined energy of the photons must exceed the ionization energy, and ionization may occur by direct excitation to the continuum or by an autoionizing resonance. The internal energy of the ion can be established from energy balance, provided the energy of the photoelectron is known.

The techniques mentioned so far are used to populate atomic or molecular levels with no or little thermal population in the beam. State-selective collision experiments involving low-lying thermally populated levels can be conducted by state-selective depletion of level population. In this scheme molecules in a specific level are
labeled rather than selected. Labeling can be done by excitation to a bound electronically excited state, with the subsequent fluorescence predominantly populating other vibrational levels (Bergmann et al. 1980; see Fig. 12.2a), or by selective photodissociation (Ling and Wilson 1976; see Fig. 12.2b). If excitation is done with polarized light, molecules in different \( m \) states are pumped out of the level at a different rate, leaving the depleted ensemble aligned (de Vries, Srdanov, Hanrahan, and Martin 1983; Snels, Geraedts, Stolte, and Reuss 1985; Heffer, Ziegler, Mattheus, Fischer, and Bergmann 1986).

Molecular beam experiments with state selection by means of selective population or depletion require a sufficiently high population in the level that absorbs the first photon. The cooling of internal degrees of freedom in supersonic expansions is vital, in most cases, to establish a sufficiently high population density. However, cooling limits the range of rotational quantum numbers accessible with this technique, because only low \( j \) levels are populated and \( j \) changes, at most, by 1 quantum per absorbed or emitted photon. The range of vibrational levels accessible by selective population is not limited by fundamental principles. It is merely determined by the variation of the relevant Franck-Condon factors with \( v^* \).

### 12.2 Molecular State Selection by Population Depletion

State selection can be achieved by labeling molecules in a specific subgroup of quantum states by population depletion through optical pumping. The desired signal is obtained by taking suitable differences of the scattering signal with the pump laser off (\( I_{0s} \), all thermally populated levels contribute) and the pump laser on (\( I_{os} \), the contribution of the depleted level is missing). In crossed molecular beam experiments, it is advisable to measure both \( I_{0s} \) and \( I_{os} \) with the target beam on and off. By again taking suitable differences, the background signal resulting from scattered light and scattering off the residual gas can be eliminated. A detailed discussion of the data collection procedure and relevant rate equations is given by Bergmann et al. (1980).

#### 12.2.1 Rotational and Vibrational State Selection

**12.2.1.1 The Concept.** Population depletion is most easily applied when the relevant excitation kinetics scheme can be described by an equivalent three-level system (Fig. 12.2a) with a 2→1 and 2→3 branching ratio that favor the latter transition. This occurs if the bond distances of the ground and electronically excited states are different and the Franck-Condon factors are also relatively large for \( \Delta v > 0 \) transitions. In this section, orientation and alignment effects are disregarded. Consider the population in a given \((v, j)\) state summed over all \( m \) levels. Also, the molecules are exposed to unpolarized light. In this case, the solution of the \( m \)-averaged rate equations (see Chapter 9) applies, and the fractional depletion of level 1 can be determined provided the laser intensity, \( I \), electronic lifetime, \( \tau \), and Franck-Condon factor, \( F_{1s} \), are known. The excitation probability or fractional depletion of the pumped levels at various reduced times \( T = t/\tau \) (\( \tau \) is the electronic lifetime) is shown in Fig. 12.3 for a fixed \( \tau \) but varied product of Franck-Condon and Hönl-London factors,
Figure 12.3  Variation of the excitation probability, $E$, in a three-level system as a function of the product of Franck-Condon and Hön-London factors, $T_{12} \cdot H_{12}$, for different reduced times, $T = t/\tau$, where $\tau$ is the electronic lifetime. $E$ is proportional to the relative population $N_3$ in level 3. For $T_{12} \cdot H_{12} \rightarrow 0$, $E$ is small because of the small $1 \rightarrow 2$ transition probability. For $T_{12} \cdot H_{12} \rightarrow 1$, $E$ is small because of the vanishing $2 \rightarrow 3$ decay rate.

$T_{12} \cdot H_{12}$. The pumping is inefficient for $T_{12} \rightarrow 0$ (ground and electronically excited states have significantly different bond length) and $T_{12} \rightarrow 1$ (the shape and equilibrium distance of both electronic states are very similar). In the former case, the excitation probability on the given transition is very small, and efficient population transfer out of level 1 requires a relatively high laser intensity. In the latter case, the transfer rate to the third level is small. This is strictly true only for $Q$ line excitation in a homonuclear molecule with only $Q$ line emission. In this situation, population transfer out of level 1 can be achieved if the molecule is exposed to the laser radiation for times $\Delta t \gg \tau / T_{12}$. In all other cases ($P$ or $R$ excitation or heteronuclear molecules), the pumped level will be depleted even for $T_{12} \rightarrow 1$ but the population will be redistributed only to neighboring rotational states by $P$, $Q$, or $R$ emission. An example of efficient state labeling by population depletion is given for a favorable system (Na$_2$) in Fig. 12.4. The pump laser is tuned across the $A'$ $\Sigma_+^+(v' = 0, j' = 28) \rightarrow A' \Sigma^+_2(v' = 9, j' = 27)$ resonance. The population of the $(v'' = 0, j'' = 28)$ level is monitored by observing the fluorescence induced from this state by a probe laser further downstream. With the pump laser at resonance, less than 1% of the thermal population remains in that level. Applications of this technique to the study of rotational energy transfer are discussed in Chapter 24.
12.2.1.2 Line Shape Problem. State-selective experiments can be conducted with a modulation efficiency $P_M = (n^\sigma - n^\omega)/n^\sigma < 1$. Here $n^\sigma$ and $n^\omega$ are the population of the level under consideration with the pump laser off and on, respectively. The best signal-to-noise ratio, however, is achieved for $P_M = 1$. Molecules, with increasing velocity components, $v_\perp$, perpendicular to the beam axis are pumped less efficiently because their absorption frequency is Doppler shifted out of resonance. A high degree of modulation can be maintained only for molecules flying inside a cone of full angle $\alpha_\perp$ given by

$$\sin \alpha_\perp = \frac{\lambda}{v} \Delta \nu_\perp \quad (12.1)$$

where $\Delta \nu_\perp$ is the width of the absorption line, and $\lambda$ and $v$ are the wavelength of the pump laser and the molecular velocity, respectively. For optimum signal-to-noise ratio, it is advisable to collimate the molecular beam to an angle of $\approx \alpha_\perp$. With $\Delta \nu_\perp = 20$ MHz, $\lambda = 600$ nm, and $v = 10^3$ m/s, equation (12.1) gives $\alpha_\perp = 0.7^\circ$. In favorable cases, the molecular transition can be strongly saturated and the population in a particular level can be depleted for a larger range of $v_\perp$. An example, taken from Heffer et al. (1986), is given in Fig. 12.5, which shows the fluorescence intensity of Na$_2$ induced by a probe laser downstream of the pump laser. At resonance, a power of $\leq 1$ mW is sufficient to pump 15% of the molecules out of the level ($v^\omega = 0, j^\omega = 3$). With a pump power of 210 mW, all molecules with a Doppler-shift of up to 100 MHz (corresponding to a cone $\alpha_\perp \leq 7^\circ$) are pumped with an efficiency of $P_M = 1$, although in this particular case the natural line width is only 25 MHz (Demtröder, Stetzenbach, Stock, and
Figure 12.5 Saturated optical pumping is apparent from the variation of the probe-laser-induced fluorescence as the pump laser is tuned across the resonance further upstream. The polarization vectors $\vec{e}_1$ and $\vec{e}_2$ of the two lasers are parallel. Both lasers excite the $(v^* = 0, j^* = 3) \rightarrow (v^* = 9 \rightarrow j^* = 4)$ transition in Na$_2$ ($X^1\Sigma^+_u^0 \rightarrow A^1\Sigma^+_u^0$). [Reproduced from Hecht et al. (1986).]

Witt 1976). Unlike the case of a two-level system (Citron, Gray, Gabel, and Stroud 1977), in this three-level system drastic deviation from a Lorentzian lineshape is observed for high pump rates.

12.2.1.3 Modulation of Other Levels. Population depletion by bound–bound transitions leads to population enhancement of neighboring levels by spontaneous fluorescence. Figure 12.6 gives an example. The pump laser is tuned across the resonance of the $P(v^* = 0, j^* = 7)$ and $R(v^* = 0, j^* = 11)$ transition to the $^3\Sigma_u^+(v^* = 17)$ level of Na$_2$. The probe laser monitors the population of the level $(v^* = 3, j^* = 13)$. Excitation of the $j^* = 11$ level results in a fourfold enhancement of the $(v^* = 3, j^* = 13)$ level population by subsequent $P$-branch fluorescence.

Modulation of the population of a vibrational level is intolerable in most reactive scattering experiments. Reaction cross sections may be enhanced significantly by vibrational excitation (Odiorne, Brooks, and Kasper 1971). Thus, even a small population enhancement may dominate the number of product particles formed. Such problems are not incurred with the technique of population depletion by means of photodissociation (see section 12.2.3). They are less critical for the study of inelastic collisions (see Fig. 12.7). Depletion of the rotational level $j = i$ in $v^* = 0$ results in a reduction of the scattering rate observed by monitoring the flux of molecules at the scattering angle $\theta$ in the level $j = f$ (see Fig. 12.7a). Simultaneously, the population of levels $j = i + 2$ (assuming pumping on an $R$ transition) in the levels $v^* = 0$ and $j = i + 2$, as well as $j = i$ for $v^* > 0$, is enhanced, leading to an increase of the scattering rate from these levels into the level $f$.

The relative magnitude of the relevant cross sections and Franck–Condon factors determines whether or not the parasitic modulation of other levels causes a problem in the signal analysis. The corresponding rate equations are discussed in detail by Bergmann et al. (1980) for rotational excitation and by Gottwald, Matteus, Bergmann, and Schinke (1986) for combined rotational–vibrational excitation. What matters in the case of rotationally inelastic scattering is essentially the following products

Figure 12.6 Population enhancement by optical pumping. The pump laser frequency is tuned and excites the $(v^* = 0, j^* = 11)$ and $(v^* = 0, j^* = 7)$ levels of Na$_2$ on an $R$ and a $P$ line, respectively, whereas the population in the level $(v^* = 3, j = 13)$ is monitored further downstream by a probe laser. P-branch emission following $R11$ excitation significantly enhances the population in the probed level.
Figure 12.7  Parasitic modulation of neighboring levels in state selection by the optical pumping scheme. Level $i$ is pumped and level $f$ is probed. The heavy arrow indicates the collisional energy transfer path under investigation. The wavy arrows represent spontaneous decay pathways, and the striped arrows give the collisional coupling to the level $f$ resulting from level modulation by spontaneous emission: (a) for rotationally inelastic collisions; (b) for vibrationally inelastic collisions, in which parasitic modulation is a more severe problem.

of Franck–Condon factors and ratio of cross sections

$$X_{oo} = F_{20} H_{k+2} \frac{\sigma_{11}(\theta)}{\sigma_{01}(\theta)}$$  \hspace{1cm} (12.2a)$$

$$X_{v'0} = F_{2v'} H_k \frac{\sigma_{v'v}(\theta)}{\sigma_{0v}(\theta)}$$  \hspace{1cm} (12.2b)$$

The upper and lower indices refer to the vibrational and rotational quantum numbers respectively, and $k = i + 2$ and $i$. The Hoenl–London factors, $H_k$ (Hertzberg 1950), are of the order of 0.5. The parasitic modulation transfer within the same vibrational level is given by $X_{oo}$, whereas $X_{v'0}$ gives the contribution from levels $v' > 0$. The ratio of cross sections in the former is of the order of unity, thus $X_{oo}$ is small if pumping occurs on a transition with a small Franck–Condon factor $F_{20}$. Typically, because $\sigma_{11}(\theta) \ll \sigma_{01}(\theta)$, $X_{v'0}$ is a small quantity independent of the value of $F_{2v'}$. Parasitic modulation transfer is a more significant problem for vibrational excitation, for example, $v'' = 0 \rightarrow v'' = 1$. Here the level $i$ refers to the vibrational ground state and $f$ to the excited state (see Fig. 12.7b). The relevant quantities are

$$X_{11} = F_{11} H_k \frac{\sigma_{11}(\theta)}{\sigma_{01}(\theta)} \quad \text{and} \quad X_{v''1} = F_{2v''} H_k \frac{\sigma_{v''v''}(\theta)}{\sigma_{0v}(\theta)}$$  \hspace{1cm} (12.3)$$

The ratio of cross sections for vibrational transitions will be of the order of unity for $v'' = 2$ but decreases as $v''$ increases. Therefore, $X_{v''1}$ is small for $F_{2v''} \ll 1$. The cross section for rotational energy transfer within $v'' = 1$, however, is larger than the $v'' = 0 \rightarrow v'' = 1$ excitation cross section, and typically $\sigma_{11}(\theta)/\sigma_{01}(\theta) \gg 1$. Thus, the parasitic modulation $X_{11}$ is only small for $F_{11} \ll 1$.

Recently, angularly resolved vibrational excitation in Na$_2$–He
collisions has been studied (Gottwald, Mattheus, Bergman, and Schinke 1986). Despite a Franck-Condon factor as small as $F_{\nu\nu} = 10^{-3}$ for $\nu' = 1$, the necessary correction resulting from $X_{11}$ was substantial for small scattering angles.

12.2.4 Summary. State selection by modulation of thermally populated levels by means of optical pumping is a powerful technique in crossed molecular beam experiments. If laser-pumping molecular alignment is not desired, pumping should occur preferentially on an $R$ rather than on a $P$ or $Q$ transition (see subsequent sections). The parasitic modulation of other levels associated with this technique is a tolerable problem for rotationally inelastic scattering, but requires careful corrections in the case of vibrationally inelastic collisions. It is severe problem in reactive scattering.

12.2 Molecular Alignment and $m$ State Selection by Optical Pumping

12.2.1 Introduction. The discussion of the preceding section disregarded the fact that, in most cases, laser radiation is polarized. The pump rate depends on the orientation of the molecule's transition dipole moment relative to the laser polarization $\mathbf{E}$. Thus, the ensemble of molecules will remain aligned or oriented after interaction with a polarized laser.

Laser-induced alignment of ground state particles is a well-established technique in double resonance spectroscopy of ground state atoms and molecules (Kastler 1950; Rosner et al. 1975) and for the investigation of collisional reorientation (Drulinger and Zare 1969, 1973). It has also been observed in molecular beams (Visser, van der Meij, Bekooy, Korving, and Beenakker 1977) and was recently applied in crossed molecular beam scattering experiments (Mattheus, Fischer, Ziegler, Gottwald, and Bergmann 1986). In the next paragraph we discuss the alignment of molecules by saturated optical pumping using bound-bound transitions. Alignment of ground state species by selective photodissociation is dealt with in section 12.2.3. Application of polarized optical pumping to excited states is treated in section 12.4.2. Detection of alignment is discussed in Chapters 9 and 24.

12.2.2.2 Alignment of Ground State Molecules by Saturated Optical Pumping. The variation of the pump rate between levels $j_i$ and $j_j$ with $m$ is given by the square of the corresponding Clebsch-Gordan coefficient $(1_{q/m} j_i j_j m + q)$ (Edmonds 1957). The variation of the pump rate $W(m)$ with $m$ for $P$, $R$, and $Q$ pumping with linearly polarized light is given in Table 12.1. Using this table, the relative depopulation of $m$ levels can be determined if the laser power is sufficiently low to ensure pumping in the weak excitation regime for all $m$ levels. Also, fluorescence from the excited state back to the pumped level modifies the $m$-level population, unless the Franck-Condon factor for this transition is small. In general, a solution of the system of rate equations (see section 9.1.2) is required to determine the resulting alignment or orientation. This can be done numerically. For small $j$, analytical solutions are possible (Bussert 1986; see section 12.4.1). For large $j$, $m$-decoupling approximations, leading to analytical solutions, are justified in most cases of practical interest. An example is

<table>
<thead>
<tr>
<th>$\Delta m = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W^P(m)$</td>
</tr>
<tr>
<td>$W^R(0)$</td>
</tr>
<tr>
<td>$W^Q(m)$</td>
</tr>
<tr>
<td>$W^Q(j)$</td>
</tr>
<tr>
<td>$W^P(m)$</td>
</tr>
<tr>
<td>$W^P(0)$</td>
</tr>
</tbody>
</table>

Table 12.1 Variation of the Relative Transition Rate with $m$ for $P$, $Q$, and $R$-Pumping and Excitation by Polarized Light
given in Fig. 12.8 for Na₂ and linear laser polarization. The variation of the pump rate \( W_{R,P}(m) \) with \( m \) is very similar for \( P \) and \( R \) transitions. An important difference, however, is that \( W_R(j) = 0 \) but \( W_R(j) > 0 \). For a low laser pump power (0.02 mW), the resulting alignment is similar for both \( P \) and \( R \) pumping. At sufficiently high laser power (>2 mW), the population of all \( m \) levels is depleted in the case of \( R \) pumping. \( P \) pumping, on the other hand, depletes the population of all levels \( |m| < j \) but leaves the population in \( |m| = j \) unchanged. It is this feature that allows the preparation of a highly aligned ensemble of molecules in the limit of saturated optical pumping. \( Q \) pumping leads to the depletion of all \( m \)-levels except \( m = 0 \).

12.2.2.3 Scaling of the Solution of the Rate Equations. The stepwise analytical solution of the \( m \)-decoupled rate equations, using equations 9.87a through 9.87g (see Chapter 9, section 9.1.2), is a rather simple procedure that allows the incorporation of a realistic laser beam intensity profile (Bergmann and Gottwald 1981). Once the population distribution \( n(m) \) is obtained for a given laser pump power, the solution can be conveniently scaled to other rotational levels or pumping transitions. The fractional depletion of two levels, \( (j_1, m_1) \) and \( (j, m) \), pumped with linearly polarized light of frequency \( \omega \) and intensity \( I(j) \) on a \( P \) transition is identical, if (see Chapter 9, section 9.1.1)

\[
I(j) \left( \begin{array}{cc} j_1 & 1 \ j_1-1 \end{array} \right) S(j,j-1)
= I(j_1) \left( \begin{array}{cc} j_1 & 1 \ j_1-1 \end{array} \right) S(j_1,j_1-1) \tag{12.4}
\]

which gives

\[
I(j) \frac{j^2 - m^2}{(4j^2 - 1)} = I(j_1) \frac{j_1^2 - m_1^2}{(4j_1^2 - 1)} \tag{12.5}
\]

In particular, for \( (m_1 = 0, j_1 \gg 1) \) and \( m = 0 \), it follows that

\[
I(j) = \left( 1 - \frac{1}{4j^2} \right) I(j \gg 1) \tag{12.6}
\]

Thus, the pump laser intensity \( I(j) \) required for a given fractional depletion of the level \( (j, m = 0) \) is only weakly dependent on \( j \). \( I(j) \) rapidly approaches the asymptotic value from which it differs for \( j > 5 \) by less than 1%. It is also easy to verify that the depletion of all levels \( m > 0 \) in different \( j \) states is the same for \( m/j = m_1/j_1 \), provided equation (12.5) is fulfilled. The weak dependence of \( I(j) \) on \( j \) allows the solution of the rate equations to be scaled for a given laser intensity in the classic limit of large \( j \) to small \( j \). The solution with \( W(\theta) = W(0) \cdot (1 - \cos^2 \theta) \) for \( P \) pumping, for example, where \( \theta \) is the angle between \( j \) and \( \vec{\epsilon} \) yields the classic distribution function \( n_0[\cos^2 \theta] \) (Altkorn and Zare 1984). For \( j \geq 5 \), the population of \( m \) levels is then accurately given by \( n_0^m[(m/j)^3] \). \( R \) pumping leaves a population distribution given by \( n_0^m[(m(j + 1))^3] \), whereas \( Q \) pumping leads to \( n_0^m[1 - (m/j)^3] \) (see Table 12.1). Unless the molecular beam is highly collimated to interact only with the center of the laser beam, the determination of the \( m \)-level population requires an appropriate average over molecules passing through the center and the wings of the laser beam.
12.2.2.4 Experimental implementation and Example. A high degree of laser polarization is crucial to the successful implementation of the saturated optical pumping technique. For single level preparation, the population of the level $|m| = j - 1$ must be depleted. Consequently, the pump laser intensity must significantly exceed the saturation intensity for the $m = 0$ level. For $P$ pumping, the ratio of laser intensities required to achieve the same fractional depletion of the levels $m = 0$ and $|m| = j - 1$ is given by

$$\frac{I(m = 0)}{I(|m| = j - 1)} = 1 - \left(\frac{j - 1}{j}\right)^2$$

Therefore, only a small fraction of the laser intensity with perpendicular polarization is sufficient to significantly deplete the population in the level $|m| = j$.

In their experiment, Hefter et al. (1986) focused the output of a single-mode polarization-preserving fiber (intensity ratio $I_0: I_\perp = 10^5$) into the interaction zone with the molecular beam. The direction of the linear laser polarization $\hat{e}$ is changed by rotation of a $\lambda/2$ plate inside the vacuum chamber. A high degree of laser polarization is ensured by a subsequent high-quality polarizer that rotates at twice the speed of the $\lambda/2$ plate, synchronously with $\hat{e}$. The aligned ensemble of molecules is interrogated further downstream by a second laser that excites the molecules near the limit of saturation as well. The fluorescence is collected with a detector in the magic angle arrangement (see Chapter 9, section 9.1.1) to ensure a detection efficiency independent of the orientation of the molecule. If the pump of the probe laser excites the molecules in the limit of weak excitation ($E \ll 1$), the detector response would follow the functional form $(1 + a \sin^2 \beta)$. If both lasers excite the molecule in the limit of saturation, the signal should vary with $\beta$ (see section 9.1.5 and Fig. 9.5).

$$\frac{I(\beta)}{I_{\text{max}}} = \left[1 - \left(\frac{1}{2}\right)^{j-1}\right]^{-1} \left[1 - \left(\cos \frac{\beta}{2}\right)^{j-1} - \left(\sin \frac{\beta}{2}\right)^{j-1}\right]$$

(12.7)

This function is plotted in Fig. 12.9 for $j = 1$ and $j = 28$. Here, $I(\beta)$ is zero for $\beta = n\pi$ ($n = 0, 1, \ldots$) because for these angles the probe laser interacts only with those levels, the population of which is depleted by the pump laser. As soon as $\beta \neq n\pi$, most of the population of the level $|m| = j$ with respect to pump laser polarization $\hat{e}_1$ transfers to $|m| < j$ with respect to the probe laser polarization $\hat{e}_2$. Levels $|m| < j$ are detected with uniform detection efficiency in the given arrangement. The experimental result (Fig. 12.9) is similar to the expected response. There are, however, two significantly different features. First, the experimental result shows a shoulder near $\beta = 30^\circ$ and $210^\circ$. This shoulder is related to the alignment of the molecules induced by the supersonic flow (Sinha, Caldwell, and Zare 1974; Visser, Bokoo, and Corving 1977; see also Chapter 9, section 9.1.5). For an isotropic distribution of molecular momenta prior to interaction with the beam, these shoulders would disappear. Second, $I(\beta = n\pi) \neq 0$ is observed in contrast with the calculated result. The residual intensity results from mixing of $m$ levels resulting from hyperfine precession along the flight path from the pump laser to the detector (see Fig. 12.10). A minor contribution to the residual signal stems from incomplete pumping of those molecules that

![Figure 12.9 Calculated variation of the detector response (equation (12.7)) with saturated P pump and saturated P probe (dashed lines) for j = 28 and j = 1. The solid line is an experimental curve for j = 28. The probe laser polarization forms the magic angle $\gamma_m$ with the detector's axis of symmetry. The decrease in the observed signal near $\beta = 60^\circ$ and $240^\circ$ is caused by the flow-induced molecular alignment upstream of the pump laser. Hyperfine mixing of m levels causes $I(\beta = 0)$ to be nonzero. [Reproduced from Hefter et al. (1986).]
reach the detector. Hyperfine mixing imposes a fundamental limitation on the $|m|\text{-level state purity that can be achieved. This is most obvious for } j = 0 \text{ (see Fig. 12.11), but is also evident for } j = 28.$

12.2.2.5 Limitation of the $m$-Level State Purity. Rotating molecules, including those in a $^1\Sigma$ state, have a magnetic dipole moment. An external magnetic field $B$ will cause a precession of the molecular angular momentum around $B$. The result is a mixing of the $m$-level population. A sufficiently strong external field applied in the direction of the axis of symmetry of the angular momentum distribution, however, will cause the $j$ vector to precess around $B$ without changing the $m$-level population. In fact, with such a field the $m$-level distribution will be less susceptible to stray magnetic fields (Gupta 1980; Engelke and Meiwes-Broer 1984). Trefers and Kowting (1983) made use of an external magnetic field to reorientate the molecules before detection by laser-induced fluorescence with spatially fixed laser polarization. The precession angle is given by

$$\beta = gJ \frac{\mu_B B}{\mu} \frac{L}{v} \quad (12.8)$$

where $g_J$ is the rotational $g$ factor, $L$ the length over which the magnetic field is applied, and $v$ the velocity of the molecule. With $L = 50$ mm, a magnetic field of about $2 \times 10^{-5}$ $T$ and $2 \times 10^{-2}$ $T$ was sufficient to rotate the angular momenta of $I_2$ and Na$_2$, respectively, by $90^\circ$ in the plane perpendicular to $B$. Thus, external fields can be used to control the axis of symmetry of the molecular alignment. In most cases, shielding of external fields will be required to prevent the molecular angular momentum from precessing.

Precession resulting from hyperfine interaction imposes a more fundamental limit on the $m$-level state purity. This is a problem particularly for small $j$ levels (Allkorn, Zare, and Greene 1985). For saturated optical pumping the probe laser-induced fluorescence (with pump and probe laser polarization being parallel) $I(\beta = 0)$ is proportional to the population in levels $|m| < j$ populated by hyperfine precession. The scrambling of $m$ levels decreases with increasing $j$ (see Fig. 12.11). Assuming complete dephasing of the precession angle along the flight path between pump and probe, the expected fluorescence intensity including hyperfine precession is (see Chapter 9, section 9.1.5)

$$\frac{I(\beta = 0)}{I_{\text{max}}} = \frac{2}{2j - 1} (1 - \langle jj | jj \rangle^2 + \langle jj | j - j \rangle^2) \quad (12.9)$$

The mixing of $m$ levels is calculated by expanding $|jm\rangle$ in the basis $|FM_F\rangle$, where $F$ and $m_F$ refer to the total angular momentum, with subsequent projection onto the final $|jm'\rangle$ states. Assuming complete dephasing along the path between pump and probe laser, the result is

$$\langle jm' | jm \rangle^2 = N(j) \sum_{F, M_F} (jm' | IM_F - m' | FM_F|^2 \cdot (FM_F, IM - M_F | jm) = (12.10)$$

For the homonuclear molecule, Na$_2$, with an atomic nuclear spin, $I_a = 3/2$, the sum over the combined nuclear spin, $I$, of the molecule is restricted to even values if $j$ is even and to odd values...
if \( j \) is odd. The factor \( N(j) \) ensures appropriate averaging according to the statistical weight of a given level. For \( \text{Na}_2 \), it is found that \( N(j) = 1/10 \) for odd \( j > 1 \) and \( N(j) = 1/6 \) for even \( j \) and for \( j = 1 \). The last term of equation (12.9) accounts for the fact that for \( j \leq I \), a fraction of the population in \( m = -j \) couples to \( m = +j \) and is thereby not lost from the population \( |m| = j \).

The signal calculated from equations (12.9) is also included in Fig. 12.11 (open circles), and excellent agreement is found. Experimental and calculated data exhibit an undulating structure with the minimum and maximum signal for even and odd \( j \) values being slightly below and above the average trend, respectively. This occurs because in \( \text{Na}_2 \) even \( j \) levels couple to the total nuclear spin \( I = 0 \) and 2 while odd ones couple to \( I = 1 \) and 3. The larger maximum spin causes a somewhat more effective mixing of \( m \) levels in the latter case.

12.2.2.6 Application: Rotationally Inelastic Scattering of \( |m| \)-Selected Molecules. Matthey et al. (1986) have applied the \( |m| \)-selection technique described in the preceding to rotationally inelastic differential scattering of \( \text{Na}_2 \)-rare gas collisions. They were able to verify experimentally the theoretical conjecture (Eckelt and Korsch 1977; Schinke and Korsch 1980; Khare, Kouri, and Hoffmann 1981, 1982) that the direction of momentum transfer \( \Delta \mathbf{k} \) is a relevant quantization axis along which \( m \) is preserved in rotationally inelastic collisions involving repulsive interaction. A typical result for the \( \text{Na}_2 \)-Na collision system is discussed here briefly. Further examples are given in Chapter 23.

The flux of \( \text{Na}_2 \) molecules in the level \( j = 0 \) is determined in the scattering plane at the scattering angle \( \theta_{\text{LAB}} \) (Fig. 12.12). Saturated \( Q \) or \( P \) pumping prepares molecules with their angular momentum parallel to the scattering plane but perpendicular or parallel to the laser polarization \( \vec{\ell} \), respectively. The former is determined by the axes of the \( \text{Na}_2 \) and the neon beam. The technique described in section 12.2.1.1 is applied to isolate

![Figure 12.11](image1)

Figure 12.11 Minimum probe laser signal for \( \beta = 0 \)
(pump and probe laser polarization are parallel). With increasing \( j \), \( I(\beta = 0) \) decreases because mixing of \( m \) levels becomes less important. The undulating structure results from the fact that even and odd \( j \) levels mix with \( I = 0, 2 \) and \( I = 1, 3 \). The larger nuclear spin in the latter case causes a more efficient mixing and results in a higher minimum intensity. [Reproduced from Hefter et al. (1986).]

![Figure 12.12](image2)

Figure 12.12 Newton diagram for the scattering of \( |m| \)-selected molecules. The scattering signal is observed at the angle \( \theta_{\text{LAB}} \) as the pump laser polarization \( \vec{\ell} \) is rotated in the scattering plane. The direction of momentum transfer forms an angle \( \theta_{\Delta k} = 67° \) with the molecular beam axis \( \vec{z} \) for the \( j_i = 6 \rightarrow j_f = 0 \) transition.
Figure 12.13 Variation of the scattering signal for the $j_i = 6 \rightarrow j_f = 0$ rotationally inelastic transition at the rotational rainbow angle for this transition with the angle $\theta_R$ (see Fig. 12.12). Data for saturated $P$, $Q$, and $R$ pumping are given. [Reproduced from Matheus et al. (1986).]

\[ j_i = 6 \rightarrow j_f = 0 \] rotationally inelastic collisions. Saturated $R$ pumping yields the $|m|$-averaged cross section whereas saturated $Q$ or $P$ pumping yields the contribution of all levels except $m = 0$ or $|m| = j$, respectively. The flux of molecules in $j = 0$ scattered under $\theta_{LAB}$ is observed as $\theta_R$ rotates in the scattering plane. The contribution of the levels $m = 0$ or $|m| = j$ is isolated by taking the difference of the signal for $R$ and $Q$ or $P$ pumping, respectively.

For the given scattering angle, the direction of momentum transfer $\Delta k$ and the molecular beam axis form an angle of $\theta_{LAB} = 67^\circ$. Projection of the laser-prepared population distribution onto the axis $\Delta k$ leads to a population of $m'$ along $\Delta k$, given by

\[ n(m') = n(j) |d_{m,0}(\theta)|^2 \quad (12.11) \]

When writing equation (12.11), the influence of the flow-induced molecular alignment and hyperfine precession has been neglected. If $\Delta m' = 0$ is valid, the signal for $Q$ pumping should be proportional to $n(m' = 0) \sim |d_{0,0}(\theta)|^2$ because only scattered particles in $m_r = 0$ are detected.

The results for $j = 6$ are shown in Fig. 12.13. As expected, the signal for $R$ pumping is independent of $\theta_R$ but the data for $Q$ pumping show a pronounced minimum for $\theta_R = 67^\circ$. The width and depth of the experimental and calculated signal (solid line) agree very well. The latter was calculated assuming $\Delta m' = 0$ in the collision process and taking into account hyperfine mixing as well as molecular alignment prior to the interaction with the pump laser. A more detailed sensitivity analysis shows that less than 10% of the collisions involve $\Delta m' > 0$. This result provides direct experimental evidence that the direction of momentum transfer $\Delta k$ is the relevant quantization axis along which a strong propensity for conservation of $m$ in rotationally inelastic processes is valid in the limit of sudden collisions.

12.2.2.7 Summary. Saturated optical pumping on $Q$ or $P$ transitions allows one to prepare molecules in the level $m = 0$ and $|m| = j$, respectively, with respect to the linear laser polarization $\hat{e}$. A high degree of laser polarization is required for a successful application of this technique. Saturated pumping is most easily achieved for molecules crossing the laser beam near its center. Therefore, the laser beam must be sufficiently large and the subsequent collimation sufficiently good to prevent molecules that have not seen the center of the laser beam from reaching the scattering center or the detector. This limits the possibility of increasing the laser intensity for more efficient pumping by tight focusing.

The technique is applicable to molecules with transitions that can be strongly saturated with available laser sources. Thus, with pulsed lasers, it can be applied to a large class of molecules. Optical pumping is not necessarily restricted to electronic transitions. Infrared absorption, or even overtone pumping, could also be used, at least in principle. For small $j$, the selectivity of this technique is limited by interaction with the nuclear spin, which causes hyperfine precession.

For some collision experiments involving aligned molecules, the benefit of very high $|m|$ selectivity is marginal. This is true, for example, for beam–gas experiments, in which kinematic averaging would significantly reduce the $|m|$ selectivity in the center-of-mass frame. To some extent, this is also true for beam–beam
experiments. However, for crossed molecular beam experiments, such as described before, high |m|-state selectivity is vital to yield the desired information. Another example is the scattering of molecules in, \( m = 0 \) or \(|m| \neq j\) from surfaces. For example, here \( m \) is defined with respect to the normal of the surface. The \( m \)-level population distribution of scattered molecules contains information about surface corrugation (Proctor, Kouri, and Gerber 1984; Lauderdale, McNutt, and McCurdy 1984).

12.2.3 Alignment of Ground State Molecules by Photodissociation

12.2.3.1 Introduction. Orientationally selective interaction of polarized light with molecules occurs also in bound free transitions. Dehmelt and Jefferts (1962) first proposed, and later carried out (Richardson, Jefferts, and Dehmelt 1968; Jefferts 1969), experiments to align \( \text{H}_2^+ \) molecular ions by selective photodissociation. The ions were created by electron bombardment and then trapped in an RF quadrupole field. The population of molecules remaining in the trap after illumination by linearly polarized light is aligned. Later Vigué, Broyer, and Lehmann (1975) observed orientational selective predissociation of laser-excited \( \text{I}_2(\Sigma_g^+) \) molecules by an external magnetic field. They pointed out that this mechanism can be used to prepare a variable alignment and orientation of the remaining ground state molecules. Electric field-induced predissociation of \( \text{I}_2 \) has been observed as well (Dalby, Levy, and Vanderlinde 1984). Direct photodissociation as a means of preparing beams of aligned neutral molecules has been proposed by Bersohn and Lin (1969), followed by a more complete theoretical treatment by Zare (1972). Ling and Wilson (1976) proposed to exploit saturation phenomena in photodissociation, to increase the degree of molecular alignment. This approach is similar in spirit to the one discussed in section 12.2.2. It received further theoretical treatment in a recent paper by Snels et al. (1985). They applied these ideas to the selective removal of molecular dimers by vibrational predissociation following infrared absorption. The first experimental implementation of the scheme of selective photodissociation in molecular beams is described by de Vries, Srdanov, Hanrahan, and Martin (1982, 1983) and de Vries, Tyndall, Cobb, and Martin (1986, to be published).

12.2.3.2 The Concept. For symmetric top molecules (with diatomic molecules being a particularly simple class), the molecular transition dipole moment \( \mu \) lies parallel to an axis whose orientation in the molecular frame depends on the type of electronic transition (Zare 1972; see also Fig. 12.14). If \( \hat{z} \) is the axis of symmetry of the molecule, \( \hat{\mu} \) is parallel to \( \hat{z} \) for \( \Delta \Omega = 0 \) (e.g., \( \Sigma-\Sigma \)) transitions (called parallel transitions) but perpendicular to \( \hat{z} \) for a \( \Delta \Omega = 1 \) (e.g., \( \Sigma-\Pi \)) transition (perpendicular transitions). Perpendicular transitions have their dipole moment perpendicular to \( \mathbf{N} \), the angular momentum of the nuclei for \( P \) and \( R \) transitions but parallel to \( \mathbf{N} \) for \( Q \) excitation. Molecules with their axis of symmetry oriented so that \( \mu \) lies parallel to the linear polarization, \( \hat{\varepsilon} \), of the laser are removed from the beam by photodissociation at the fastest rate. Molecules with \( \hat{\mu} \) in a plane perpendicular to \( \hat{\varepsilon} \) will remain unaffected. The details of the

Figure 12.14 Orientation of the transition dipole moment for various types of transitions.
dynamics of the dissociation process (see Zare 1972) are irrelevant in this context, provided the separation of the atoms is sufficiently fast to prevent any substantial radiative repopulation of the molecular ground state.

In practice, the interaction time of the molecules with the laser light is long compared with the rotation period of the molecule. Therefore, the absorption probability depends on the angle between the plane of rotation and laser polarization. It is most convenient to characterize its angular variation with respect to the angle \( \theta \) between \( j \) and \( \hat{e} \). In the limit of weak excitation and including \( P, R, \) and \( Q \) branches, the angular variation of the probability of dissociation (see, e.g., Bersohn and Lin 1969; Snels et al. 1985) is

\[
f_\text{p}(\theta) = \frac{1}{2} (1 - \cos^2 \theta) \kappa \tag{12.12}
\]

for parallel transitions, but

\[
f_\text{c}(\theta) = \frac{1}{4} (1 + \cos^2 \theta) \kappa \tag{12.13}
\]

for perpendicular transitions. With \( \kappa = 3/2 \), the normalization is such that \( \int_0^{\pi} f(\theta) \sin \theta \, d\theta = 1 \), while the average value of \( f \) is unity for \( \kappa = 1 \). The distributions of equations (12.12) and (12.13) will be observed in the limit of large \( j \), where \( \cos \theta = m/j \) is valid. The population \( n(m) \) of an individual level disappears at a rate given by

\[
\frac{dn(m)}{dt} = -\sigma(m) \phi n(m) \tag{12.14}
\]

where \( \phi \, \text{m}^{-2} \text{s}^{-1} \) is the photon flux. The absorption cross section \( \sigma(m) \) includes the sum over all transitions that are possible at the given laser frequency. Excitation to more than one continuum may occur, and both parallel and perpendicular transitions may contribute. For a diatomic or linear polyatomic molecule, the following equation may be written:

\[
\sigma(m) = 3\sigma_{||,\perp}[S_{||,\perp}^p + (S_{||,\perp}^q)^2 + (S_{||,\perp}^r)^2] \tag{12.15}
\]

The factor 3 must be included if the absorption cross section for parallel and perpendicular transitions, \( \sigma_{||} \) and \( \sigma_{\perp} \), respectively, is measured for unpolarized light. The line strength factors for \( P, Q, \) and \( R \) transitions are given in Table 12.2. The corresponding line-strength factors for symmetric top molecules with a non-vanishing quantum number, \( K \), for the projection of the angular

**Table 12.2** Line Strength Factor for Photodissociation of a Diatomic or Linear Polyatomic Molecule through Parallel or Perpendicular Transitions (see Fig. 12.14)

<table>
<thead>
<tr>
<th>P</th>
<th>Q</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{</td>
<td></td>
<td>}^p )</td>
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<tr>
<td>( S_{</td>
<td></td>
<td>}^q )</td>
</tr>
<tr>
<td>( S_{</td>
<td></td>
<td>}^r )</td>
</tr>
</tbody>
</table>
momentum on the molecule fixed axis are given by Snels et al. (1985).

The fraction of molecules remaining in the level after the interaction time, Δt, with the laser is given by

\[
\frac{n(m, Δt)}{n(m, 0)} = \exp [-σ(m)F]
\]

(12.16)

with total photon flux \( F = \int \phi(t) dt \). In practice, the photon flux is spatially inhomogeneous, and equation (12.15) must be averaged over the cross section of the laser beam.

Excitation of a parallel transition will lead to depletion of molecules with \( j \) in a plane parallel to \( \hat{e} \) (\( θ = 90° \)) but leave the population of those molecules with their angular momentum parallel to \( \hat{e} \) (\( θ = 0° \)) unchanged. Perpendicular transitions lead to a dissociation of molecules with \( j \) parallel to \( \hat{e} \) as well as perpendicular (see Table 12.2). The former disappear at a faster rate.

Figure 12.15 gives the population distribution of \( m \) levels for both parallel and perpendicular transitions for a product \( αF = 0.2 \) and \( αF = 2 \) [see equation (12.16)] typical for the experiment of de Vries et al. (1983) involving the IBr molecule. Figure 12.16 shows the total number of molecules remaining undissociated as a function of the laser fluence (in joules per square meter). These curves are calculated by Snels et al. (1985) for vibrational predissociation of \( (SF₂)_2 \) dimers. The orientational dependence of the cross section leads to a nonexponential time dependence of the remaining population. This occurs because the fraction of molecules with favorable orientation for dissociation decreases in time. For parallel transitions, the alignment is more efficient [see Table 12.2 and equation (12.15)], and thus deviation from the exponential behavior is more pronounced. Within the limit of saturation and a pure parallel transition, the fraction of particles remaining in a given \( j \) level is \( 2/(2j + 1) \).

Unfortunately, photodissociation may occur by means of excitation to more than one continuum (see, e.g., Ling and Wilson 1976). Therefore, at a given wavelength of the laser, both parallel and perpendicular transitions may contribute. In that case, the resulting alignment depends on the relative strength of the various transitions. Population depletion will be observed for all angles, \( θ \). This is particularly important if saturation phenomena are to be exploited. Then, a compromise between degree of alignment and signal level (i.e., total number of molecules remaining in the beam) is needed.

12.2.3.3 Example. The technique of alignment by selective photodissociation was applied by de Vries et al. (1983) to study the chemiluminescent reaction

\[
Xe(\text{P}_2, \lambda) + \text{IBr} \rightarrow Xe\text{Br}^* + I
\]

(12.17)

and by de Vries, Tyndall, Cobb, and Martin (1987); to study fragmentation and Penning ionization in the collision system

\[
\text{Ar}(\text{P}_2, \lambda) + \text{CS}_2 \rightarrow \text{Ar} + \text{CS}^* + \text{S}
\]

and

\[
\text{Ar}(\text{P}_2, \lambda) + \text{CS}_2 \rightarrow \text{Ar} + \text{CS}^* + \text{S} + e
\]

(12.18)

The absorption cross section of IBr at the wavelength \( λ = 532 \text{ nm} \) of the frequency doubled Nd-YAG laser is \( 8.1 \times 10^{-19} \text{ cm}^2 \). At this
wavelength 90% of the transitions have parallel character. The laser dissociates IBr molecules, emerging from an effusive multichannel array shortly before they reach the beam of metastable Xe* atoms. The latter are drawn from a cold discharge source. Actually, the laser beam overlaps partially with the collision region. A typical signal obtained with a fluence of 740 ml/m² (σ · F = 1.6) is shown in Fig. 12.17. The XeBr* chemiluminescence is reduced instantaneously as the laser is fired, because some IBr molecules in the scattering center are dissociated. The signal decreases further as the IBr molecules move from the center of the laser beam, where dissociation has been most efficient, to the collision region. Later, an increasing number of nondissociated molecules react with the xenon beam and the original signal level of the chemiluminescence is restored. The recovery time of the signal is rather long because the velocity distribution in the effusive IBr beam is broad. The maximum depletion of the chemiluminescent intensity is plotted in Fig. 12.18 for various orientations, θ_{LAB} or θ_{CM}, of the laser polarization and the xenon beam or the most probably velocity of the collision pair, respectively. The observed variation results from the combined effect of the change in the approach geometry of the collision and the change of the anisotropic distribution of emitted photons. Only if the XeBr* angular momenta were isotropically oriented for all approach geometries would the signal depend solely on IBr orientation before the collision. Taking this into account the authors conclude that a xenon atom approaching in the plane of rotation of the IBr molecule leads more efficiently to chemiluminescence than the approach parallel to the angular momentum of IBr.

Pronounced polarization effects are indicative of geometric restrictions in the approach channel. Thus, intuitively, they are expected to be seen more easily in processes with small cross sections. This experiment confirms that polarization effects are readily observable for collision systems with relatively large cross sections as well.

12.2.3.4 Comparison with the Optical Pumping Scheme and Summary. Molecular alignment by selective photodissociation differs in several respects from the optical pumping approach (see section 12.2.2). In the former case, the excited molecules are removed from the beam. Thus, problems associated with the parasitic modulation of the population in other molecular levels (see section 12.2.1.3) are not incurred. This is a distinct advantage for reactive scattering experiments in particular. Because excitation involves a continuum, individual rotational and vibrational levels are not selected, in contrast to the optical pumping scheme. In many cases, this is actually an advantage, because the laser interacts with a larger fraction of the molecules in the beam, and the signal level is higher.

Selective photodissociation does not require narrow band lasers and pulsed lasers can be used effectively. This helps to offset the disadvantage that the cross section for bound-free transitions is typically several orders of magnitude smaller than for bound-bound transitions. Unlike for beams of CW lasers, the spatial intensity profile of most pulsed lasers is often not very well characterized. If saturation phenomena are important, it is
inappropriate to calculate the achieved alignment from the average laser intensity. From the variation of the total chemiluminescence with the laser power, de Vries et al. (1983) found their results to be best described by assuming that a fraction, $f$, of molecules see the average laser power whereas the fraction $(1-f)$ does not interact with the laser at all. A fit procedure yielded $f = 0.55$ for their experimental conditions.

Experimental verification of the achieved alignment requires the interrogation of the aligned ensemble with a second laser. Observation of the angular distribution of photofragments is another, though less direct, method (Ling and Wilson 1976). Details of the dissociation dynamics come into play and reduce the sensitivity of fragment angular distribution to the alignment of the parent molecules.

The relatively high laser power needed for selective photodissociation demands a careful analysis of the possible influence of other processes, such as electronic excitation or photonization of one of the collision partners or reaction products.

With even more powerful lasers becoming available, it is conceivable that nonresonant two-photon dissociation (Zare 1972) or resonantly enhanced multiphoton dissociation or ionization can be used to align molecules for collision experiments. In the latter case, rotational–vibrational state selectivity can be regained. The ionization or dissociation step, however, should be sufficiently fast to prevent radiative decay to the electronic ground state.

The inherent limitation of $m$-state purity resulting from the nuclear spin–induced hyperfine precession, discussed in section 12.2.2.5, applies here also. The necessity to establish the degree of molecular prealignment in the beam upstream of the interaction region with the dissociating laser is strongly emphasized. Substantial flow-induced alignment has been observed for alkali beams and I$_2$ beams (Sinha et al. 1974; Visser et al. 1977; Sanders and Anderson 1984; Hefter et al. 1986). Molecules are found to have their angular momentum preferentially aligned perpendicular to the molecular beam axis. Flow-induced alignment is expected to be present in other molecular systems as well. It will result in a modulation of the subsequent scattering signals as the laser polarization $\hat{e}$ rotates, even in the absence of any polarization effects in the collision process or detection system.

12.2.4 Combined Internal State and Velocity State Selection

A subgroup of molecules in a given internal state and with a narrow range of velocities can be labeled when the population depletion technique (section 12.2) and the Doppler-shift method (Chapter 9, section 9.1.6) are combined. The laser beam may approach the molecular beam at an angle $\theta < 90^\circ$ instead of a right angle. Then only the subgroup of molecules around

$$v_\parallel = \frac{\omega - \omega_0}{k \cos \theta} \tag{12.19}$$

is labeled. Here $v_\parallel$ is the velocity component along the molecular beam axis, $k = 2\pi/\lambda$, and $\omega_0$ is the laser frequency at resonance. The velocity resolution is discussed in Chapter 9, section 9.1.6. The attainable velocity resolution depends on the angle $\theta$, the excitation wavelength, the natural line width of the molecular transition, $\Delta \nu_m$, and the collimation angle $\alpha$. Typically, a resolution $\Delta v_\parallel / v_\parallel$ of a few percentage points can be achieved.

---

**Figure 12.17** Chemiluminescence signal from the reaction in equation (12.17), as a function of the time after the laser pulse. The broken line indicates the signal level with laser off. The decrease in the signal is instantaneous because the laser partially overlaps with the scattering center (see inset) [Adapted from de Vries et al. (1983), with permission.]

**Figure 12.18** Minimum chemiluminescence signal after the laser pulse as a function of the angle $\theta_{LAB}$ between laser polarization $\hat{e}$ and the Xe$^+$ beam. The angle $\theta_{CM}$ between the light vector and the most probable Xe$^+$ + IBr relative velocity vector is indicated in the top scale. [Reproduced from de Vries, Srđanov et al. (1983), with permission.]
This velocity selection scheme has been applied to collision experiments in the bulk (Smith, Brunner, and Pritchard 1981; Smith, Scott, and Pritchard 1984). No application to molecular beam scattering appears to have been reported so far. One reason for this is that a velocity resolution of $\leq 10\%$ is readily achieved by supersonic expansion in a carrier gas. Velocity resolution of only a few percentage points, however, requires seeding in helium with very high stagnation pressure (Brusdeylins, Meyer, Toennies, and Winkelmann 1977; Toennies and Winkelmann 1977; see also Chapter 2). One specific example of high-velocity resolution in a particular quantum state should be mentioned. Steele and McFarlane (1983) applied a modified version of the technique proposed by Schuda and Stroud (1973) and Abate (1974). They used a dye laser with frequency shifting by acoustooptical modulation. The laser crosses the molecular beam axis at 90° and further downstream at an angle $\theta < 90°$. The part of the laser beam that is not shifted in frequency is used to transfer all atoms from the $F = 2$ hyperfine level of sodium ground state atoms to the $F = 1$ level by optical pumping at the first intersection. No velocity selection occurs at this step. The photons that are downshifted in frequency are used to pump molecules in a narrow range of velocities back to the $F = 2$ level. In that work, a velocity resolution of $\Delta v/v = 0.03$ for the molecules in the $F = 2$ level has been achieved.

12.3 Molecular State Preparation by Selective Population: Electronic Ground State Molecules and Molecular Ions

Vibrational state selection in molecular electronic ground states is more difficult to achieve than rotational state selection in the vibrational ground state or selection of excited atomic state. Although nonoptical methods for the production of vibrationally excited molecules are available [e.g., chemical reactions (Dzelzkalns and Kaufman 1984), electron impact (Wadehra and Michels 1985), decomposition and recombination on surfaces (Foner and Hudson 1984)], their application to molecular beam experiments will, at best, be limited to a few favorable cases.

The transition probability for direct optical $v'' = 0 \rightarrow v'' = 1$ or vibrational overtone excitation is relatively small because no electronic transition dipole moment is involved. Therefore, most studies of vibrational relaxation made use of the high particle density in the bulk. Furthermore, until very recently lasers in the near infrared were less flexible and less convenient to operate than lasers in the visible range. Excitation by means of a sequence of processes involving electronic states is either not highly selective or requires powerful lasers. The various excitation schemes will be discussed in more detail in the following.

12.3.1 Techniques Involving One Laser Photon

12.3.1.1 Infrared Excitation. The application of IR spectroscopy to molecular beam experiments using bolometric techniques is discussed in Chapter 23. Only a few crossed molecular beam or beam–gas experiments using IR excitation have been reported so far. A dramatic effect of vibrational excitation on the reaction cross section was first reported by Odiorne et al. (1971), who later extended their work to the study of rotational effects in $v'' = 1$
(Dispert, Geis, and Brooks 1979). Pruett and Zare (1976), Kurny and Zare (1978), Kurny et al. (1978), and Gupta, Perry, and Zare (1980) investigated the effect of vibration excitation of HF and DF in reaction with barium and strontium, and Hoffmeister et al. (1983) made a very detailed crossed molecular beam study of the reaction K + HF with the HF molecules excited to various $f''$ levels in $\nu'' = 1$. The influence of vibrational excitation of SF$_6$ and HF in the high-density region of the nozzle expansion was studied by Coulter, Grabner, Casson, Flynn, and Bernstein (1980) and Ellenbroek, Toennies, Wilde, and Wanner (1981), respectively. In the latter work, coaxial excitation with a CW chemical HF laser was employed. Although, the lowest rotational levels cannot be excited with radiation from a chemical laser, such limitations do not exist with F-center lasers or IR radiation generated by frequency mixing. The latter technique was used by Zacharias, Loy, and Roland (1982), Misewich, Zacharias, and Loy (1985), and Misewich and Loy (1986) to investigate the survival probability of vibrational excitation in NO($\nu'' = 1$) scattered off LiF surfaces. Very recently, Vohralik and Miller (1985) used an F-center laser in combination with bolometric detection to study resonance HF($j = 1$) + HF($j = 0$) rotational energy transfer in crossed molecular beams.

Excitation of a molecule to the ($\nu'' = 1, j''$) state results in a change of the scattering signal if the cross section for molecules in the $\nu'' = 0$ and $\nu'' = 1$ level is different. The total flux of product molecules is

$$ \hat{N} = K \sum_{\nu,j} f(v,j) \sigma(v,j;E) \quad (12.20) $$

where $f(v,j)$ is the population of the level $(v,j)$ and $\sigma$ is the cross section at the mean value, $E$, of the collision energy. $K$ combines all other factors, such as particle densities, size of the beam intersection volume, and mean relative velocity, that remain constant in a given experiment. The thermal population of levels is $f_r(v,j)$. In HF beams, the population in levels $\nu'' > 0$ is negligibly small. Excitation occurs to the level $j'' = j'' + 1$ or $j'' = j'' - 1$ for R- or P-line excitation with an excitation probability $f_{ex}(j'')$. Thus, with the pump laser off and on, the flux of product particles is

$$ \hat{N}_{off} = K \sum_{j''} f(0,j'') \sigma(0,j'';E) \quad (12.21) $$

and

$$ \hat{N}_{on} = \hat{N}_{off} + K \cdot f_{ex}(j'') \int f(0,j'') Q[\sigma(1,j'';E) - \sigma(0,j'',E)] \quad (12.22) $$

respectively. The correction factor, $Q$, accounts for the fact that the pulsed excitation leads to a pulsed flow of reaction products. The peak intensity of the latter is reduced by the spread in velocities. For endothermic reactions such as K + HCl, one has $\sigma(0,j'',E) \ll \sigma(1,j'',E)$ and the cross section is deduced from the experiment using

$$ \sigma(1,j'';E) = (\hat{N}_{on} - \hat{N}_{off}) f_{ex}(j'') f(0,j'')(KQ)^{-1} \quad (12.23) $$

The excitation probability needs to be determined separately. The procedure given by Hoffmeister et al. (1983) is discussed here. These researchers point out that the problem can be treated as the interaction of polarized monochromatic light with a two-level system (see, e.g., Steinfield 1974) despite the $(2j + 1)$ degeneracy of rotational levels. Linearly polarized light couples levels with the
same \( m \) quantum number in the lower and upper state. Spontaneous decay need not be considered because of the long radiative lifetime \((\approx 5 \text{ ms})\).

The Lorentzian profile centered on the laser frequency \( \nu_L \) and normalized to unity at the maximum is given by

\[
f_L(\nu_L, \nu, \nu) = \frac{\nu_L^2}{[(\nu_L - \nu)^2 + \nu^2]}
\]

(12.24)

where \( \nu \) is the Rabi-flopping frequency

\[
\nu = \frac{\mu_0 |E|}{\hbar} \left( \frac{J^2_m}{(4j^2 - 1)} \right)^{1/2}
\]

(12.25)

Here \( E \) is the electric field strength of the radiation and \( \mu_0 \) is the vibrational part of the transition dipole moment. At the end of the laser pulse, the relative population of the excited state for molecules of a given velocity group \((\text{corresponding to the absorption frequency } \nu)\) is given by

\[
F(\nu_L, \nu, \nu, \nu, \nu, m) = f_L(\nu_L, \nu, \nu) \sin^2 \left( \pi \left( (\nu_L - \nu)^2 + \nu^2 \right)^{1/2} \right)
\]

(12.26)

where \( \tau_L \) is the pulse duration. The fraction of excited molecules is finally obtained by integrating \( F(\nu_L, \nu, \nu, \nu, \nu, \nu, \nu, m) \) over the Doppler profile \( f_0(\nu, \nu, \nu) \) of the beam (normalized according to \( \int f_0(\nu, \nu, \nu) \, d\nu = 1 \)), where \( \nu_0 \) is the molecular transition frequency, and summation over all participating \( m \) levels. For linearly polarized light, it follows that

\[
f_e(\nu_L, \nu) = \frac{1}{2j + 1} \sum_{m=-j}^{j} \int_0^{\infty} F(\nu_L, \nu, \nu, \nu, \nu, \nu, \nu, m) f_0(\nu, \nu, \nu) \, d\nu
\]

(12.27)

Finally, this expression must be averaged over the spectral energy distribution of the laser that may vary from shot to shot. In the experiment of Hoffmeister et al. (1983), the mode separation \( \Delta \nu_k \) of the HF laser is larger than the width of the Doppler profile of the collimated beam. They assume that the cavity mode fluctuates within the interval \( \Delta \nu_k \), and arrive at the final result

\[
f_e(j) = \frac{1}{\Delta \nu_k} \int_{\nu_k-(\Delta \nu_k/2)}^{\nu_k+(\Delta \nu_k/2)} f_e(\nu_L, \nu) \, d\nu
\]

(12.28)

With a laser pulse energy of about 4 mJ and a peak intensity of about 8 kW/cm\(^2\), the excitation probability is not very sensitive to the actual laser characteristics because the transition is nearly saturated. In fact, the calculated \( f_e(j) \) was found to be within 8% of the high power limit given by \( f_{e, \text{lim}}(j) = 0.5(2j - 1)/(2j + 1) \). The high power limit is less than 0.5 because only \( 2j - 1 \) out of the \( 2j + 1 \) degenerate \( m \) levels participate in the pump process for linear laser polarization and \( P \)-line excitation.

When excitation occurs on a \( P \) transition, the angular momenta in the level \( \nu'' = 0 \) are aligned because the population in \( |m| < j \) is reduced while that of \( |m| = j \) remains unchanged. In the limit of saturation, the angular momenta are isotropically distributed in the \( \nu'' = 1 \) level. For \( R \)-line excitation, the opposite is true; that is, the excited level \( (\nu'' = 1, j') \) will be aligned.

12.3.1.2 Population by Fluorescence. Laser-induced fluorescence is a most natural path leading to vibrational excitation (see
Figs. 12.1 and 12.6). Although the technique of redistributing the population of a specific \((v^* = 0, j)\) level by means of fluorescence is not highly selective, the population distribution over levels \(v^* > 0\) depends on the level \(v^*\) in the excited state, and can thus be varied. This technique has been used in the study of differential scattering. Bergmann et al. (1980) determined the differential cross section for rotational energy transfer within \(v^* = 1\) (see also Gottwald et al. 1986). Fluorescence population of vibrational levels is particularly useful in determining integral cross sections. Fuchs and Toennies (1986) measured the attenuation of a \(\text{Li}_2(v^*)\) beam by helium and krypton for \(0 \leq v^* \leq 21\). The mean internuclear lithium–lithium distance increases in this range from \(r_e = 0.27\) nm to \(r_e = 0.35\) nm. The researchers found a non-monotonic variation of the cross section with increasing \(v^*\) of the order of 10% that results from the variation of the molecular polarizability with \(v^*\). Another interesting observation was a significant increase of the cross section for electron impact ionization with \(v^*\). McGeoch and Schlier (1986) investigated the variation of the rate of dissociative attachment in the process \(\text{Li}_2(v^*) + e \rightarrow \text{Li} + \text{Li}^-\) by low-energy electrons. They found that the rate does not vary significantly in the range between \(v^* = 10\) and \(v^* = 13\).

12.3.2 Techniques Involving Two Laser Photons

A higher selectivity in the vibrational level population is gained when two-laser photons are involved. Population transfer to a vibrational level can be achieved with a two-step stimulated emission process or by stimulated Raman scattering. In the two-step process a population in the electronic state is established, which is then transferred to the final level \(v^*\) by stimulated emission. When both lasers saturate the corresponding transitions, coherence phenomena are not important and Raman processes can be neglected, the population is shared equally between the three levels. Spontaneous decay of the intermediate, electronically excited level populates other vibrational levels and results in a loss of particles from the pump cycle. If the interaction time of the molecules with the lasers exceeds the spontaneous lifetime, the reduction in vibrational selectivity is significant.

Off-resonant—stimulated Raman scattering suffers from a loss of transition probability and vibrational tunability because only \(\Delta v^* = 1\) processes will occur. However, no population is established in an intermediate level and the vibrational selectivity is high. Near-resonant—stimulated Raman scattering is a compromise between high transition probability and high vibrational selectivity. Under favorable circumstances, laser action between the intermediate and final levels may replace the second laser. The various techniques are discussed and compared in more detail in the following.

Techniques that require coherent amplification of one or more of the photons involved in the process, such as CARS, will be less successful in molecular beam experiments because of the low density of the medium. CARS experiments have been done in the high-density region of the expansion close to the nozzle throat (see, e.g., Huber-Wälchli, Guthals, and Nibler 1979; Duncan, Österlin, König, and Byer 1981; Duncan, Österlin, and Byer 1981; Huber-Wälchli and Nibler 1982). Here, vibrational selectivity in level population will be destroyed rapidly by subsequent collisions.
12.3.2.1 Near-Resonance–Stimulated Raman Pumping: The use of near-resonance–stimulated Raman pumping in preparing highly vibrationally excited levels has been proposed and treated theoretically by DePrisco, Rabitz, and Miles (1980). The results of a detailed experimental study have been reported by Shimizu, Shimizu, and Takuma (1983, 1985). They demonstrate that high vibrational levels of Na₂ molecules can be pumped with CW lasers with powers of the order of 100 mW. Efficient and selective pumping in a two-step process must occur in times shorter than the radiative lifetime \( \tau_r \). Off-resonant pumping suffers from a loss of transition probability but \( \tau_i \ll \tau_r \), where \( \tau_i \) is the interaction time with the laser, is no longer required. As a result, the power needed for near-resonance pumping is not necessarily higher than that for efficient and selective on-resonance pumping.

The ratio of the spontaneous line width, \( \gamma_s \), and the inverse of the interaction time, \( \tau_i = \gamma_s^{-1} \), is a crucial parameter. The result of the pumping process is best described in Fig. 12.19, which gives the fraction of molecules transferred from the level \( v^r = 0 \) to the terminal level, as obtained from a density matrix calculation. Figure 12.19a and b applies to long \( (\gamma_s < \gamma_i) \) and short \( (\gamma_s > \gamma_i) \) electronic lifetimes, respectively.

With detuning of the pump (\( \omega_p \)) and stimulating (\( \omega_s \)) laser of, for example, \(-200\gamma_i\) and \(+200\gamma_i\), respectively, no population transfer occurs. When \( \omega_s \) is held fixed but \( \omega_p \) is tuned, the terminal level is populated by spontaneous emission near \( \omega_p = 0 \). For \( \omega_p = 200\gamma_i \) (i.e., \( \omega_s = \omega_p \)), Raman transitions occur. As \( \omega_p \) is tuned toward the resonance, the efficiency of the Raman process increases, reaching its maximum for \( \omega_s = \omega_p = 0 \). The enhancement over the population transfer by spontaneous emission is obvious. For \( \omega_p = 0 \), the width of the peak is essentially given by the natural line width of the intermediate level. For \( \omega_p \neq 0 \) the line width is given by the inverse of the relaxation rates of the levels in the electronic ground state. It is apparent from Fig. 12.19a that on-resonance pumping is preferable for relatively long-lived levels \( (\gamma_i \ll \gamma_s) \).

Figure 12.19b applies to short-lived states \( (\gamma_i \gg \gamma_s) \) and is calculated for stimulating laser power exceeding the pump laser power by about a factor of 40. In this case, dynamic Stark splitting occurs for \( \omega_s = 0 \). Thus, for very near-resonant pumping, the most efficient Raman process does not occur for \( \omega_p = \omega_s \). The optimum pumping efficiency is achieved for a detuning of about 8\( \gamma_i \). Experimentally determined pumping efficiencies for a various detuning \( \omega_s \) and \( \omega_p \) were found to be in good agreement with theoretical prediction.

Detuning off-resonance beyond the optimum \( \omega_{s,p} \) reduces the pumping efficiency but increases the vibrational selectivity. Figure 12.20a shows the absolute count rate of the laser induced out of the Na₂(\( v^r = 31 \)) level populated by the Raman process. The detuning \( \omega_p \) is adjusted to ensure maximum efficiency as \( \omega_s \) is changed. The left-hand scale of that figure indicates the change in vibrational selectivity. At maximum pumping efficiency, the population in the level \( v^r = 31 \) exceeds the population by spontaneous emission of all other levels by a factor of 3. This ratio approaches 10 for larger detuning at the expense of efficiency.

The optically pumped molecular beam laser that has been demonstrated for Na₂ supersonic beams (Jones, Gaubatz, Heftet, Bergmann, and Wellegehausen 1983) and I₂-supersonic beams
(Hechter, Eichert, and Bergmann 1985) is a particularly interesting version of near-resonant Raman pumping. Laser operation can be achieved with the pump laser and the dimer laser in near resonance with on-axis molecules near the transition region to free molecular flow. The population in the final vibrational level \( v'' \) of \( \text{Na}_2 \) is monitored further downstream by a probe laser behind a collimating slit on the molecular beam axis (Becker, Gaubatz, Bergmann, and Jones 1987) (see Fig. 12.20b). With the dimer laser blocked, vibrationally excited levels of the molecules near the beam axis are populated by spontaneous emission as the pump laser is tuned across the resonance. The increase in pumping efficiency and selectivity with the dimer laser operating is obvious from Fig. 12.20b. When the pump laser frequency is into resonance with molecules on the molecular beam axis, dynamic
Stark splitting occurs and the dimer laser field is shifted out of resonance. Furthermore, spontaneous decay to other vibrational levels is a major leak in the pump cycle and the transfer rate is small. Tuning the pump laser off resonance for on-axis molecules results in a significant increase in the efficiency of the population transfer. A dramatic increase in selectivity is also obvious because population by spontaneous decay is very small at a pump laser detuning of about 200 MHz.

Ideally, the molecules crossing the laser beams should experience a sequence of two consecutive \(\pi\)-pulse (see, e.g., Steinfeld 1974) in times shorter than \(\tau\), with the first pulse transferring molecules to the intermediate level while the second one stimulates them to the final state. A \(\pi\) pulse requires that \((\mu E/h) \cdot \tau = 1\), where \(\mu\) is the transition dipole moment and \(E\) the electric field strength of the laser radiation. Since \(\sqrt{\tau} \cdot \tau\) is constant for a flight path that crosses the axis of a circular laser beam at 90°, the \(\pi\)-pulse condition could be maintained across the profile of the molecular beam. The molecules typically travel only 10 \(\mu\)m during \(\tau\), and simultaneous tight focusing of the two laser beams, which can be accomplished with fiber optic components (see Chapter 9, section 9.3.1), is required. Tight focusing results, however, in a large divergence of the beam, and the condition \(t < \tau\) can be maintained only across a very small area of the molecular beam. Therefore, the total flux of molecules in the vibrational level will be small. Also, the \(\pi\)-pulse condition is fulfilled only for a given velocity group. The finite width of the velocity distribution results in a loss of efficiency and selectivity.

12.3.2.2 Off-Resonance–Stimulated Raman Pumping. The off-resonance–stimulated Raman effect is controlled by the variation of the molecular polarizability with nuclear coordinates. The coordinate variation is typically slow, resulting in a \(\Delta v = 1\) selection rule. Thus, in a molecular beam environment, the first vibrational level can be populated. The cross section for off-resonance Raman processes is much smaller than for resonance or near-resonance pumping, and powerful lasers are needed. The frequency of the lasers is not predetermined by the molecule under study, the only requirement is that the frequency difference of the two lasers match the energy difference of the molecular rovibrational levels. The tuning of only one laser allows a scan through the rotational manifold of the \(v = 1\) level. This feature makes an appropriate pair of lasers a very flexible tool, since many molecules can be pumped.

Stimulated Raman scattering in gases of simple molecules has long been established as a means of populating vibrational levels (DeMartini and Decius 1966; Devir and Bauer 1978). High detection sensitivity, which makes this technique applicable in molecular beam experiments, can be achieved by laser-induced fluorescence detection (King et al. 1983; Orr, Duval, Haines, Isenor, and King 1984) or by laser photoionization (Esherick and Owyoung 1983). A feasibility study of stimulated Raman pumping and ionization detection of \(H_2\) in a molecular beam is reported by Chandler and Farrow (1983) (Fig. 12.21). They found efficient population of the \((v = 1, j = 1)\) level of \(H_2\) with laser power of about 10 mW at 532 nm and 682 nm, focused with an \(f = 40\) cm lens. In a bulb experiment this amount of light was found to saturate the transition. Thus, tighter focusing and higher power...
could easily improve the efficiency of the pumping process. The excited molecules were detected by 2 + 1 resonant multiphoton ionization (two-photon resonance excitation followed by one-photon ionization) through the E, F state origin. Very recently Meier, Ahlers, and Zacharias (1986) used 300 mJ at 1.06 μm, together with Raman-shifted light from a H₂ or D₂ cell (λ = 1.91 μm or λ = 1.56 μm, respectively) to pump H₂ or D₂ with a transfer efficiency of the order of 30% to the ν = 1 level. The population in the pumped level, as well as in collisionally populated neighboring states, was determined by vacuum ultraviolet (VUV) (λ = 110 nm) laser-induced fluorescence from the B¹Σ⁺ state.

12.3.2.3 Stimulated Emission Pumping. Stimulated emission pumping (Kittrell, Abramson, Kinsey, McDonald, Reisner, Field, and Katayama 1981) is another method of population transfer to vibrational excited levels. Using this approach, the second laser pulse is delayed by Δt < τ relative to the first one. The first laser establishes a population in an electronically excited state; the second laser transfers the excited molecules into a vibrationally excited level by stimulated emission. Delaying the pulses avoids the influence of most coherence effects in the transfer process that depend critically on pulse-to-pulse variations in spectral, temporal, and spatial details of the laser radiation. So far, this technique has been used for spectroscopic studies in gases by observing the reduction either in sideways fluorescence (Vacca, Kinsey, Field,
and Dai 1983; Abramson, Field, Imre, Innes, and Kinsey 1985) or in the ionization yield (Suzuki, Mikami, and Ito 1985) as an indicator of the stimulation processes. Stimulated emission pumping in combination with sensitive detection techniques is also a promising technique for molecular beam experiments. It makes use of the large cross section for the absorption of resonance radiation and is not limited to the population of \( v = 1 \). The range of accessible vibrational levels is determined merely by the magnitude of the relevant Franck-Condon factors and the available laser power.

### 12.3.3 Vibrational State Selection in Molecular Ions

#### 12.3.3.1 Introduction

Molecular beam experiments with state-selected ions are not abundant yet. There are several reasons for this. Ions are less readily available in sufficiently high density because of space charge limitations. Also, detailed spectroscopic information is available only for a few simple ions of gas-phase molecules such as \( \text{N}_2^+ \) and \( \text{CO}^+ \) (Engelking and Smith 1975; see also Huber and Herzberg 1979). For those molecules, the technique discussed in section 12.2 may be applicable, provided the attainable density of ions in the beam is sufficiently high. State selection by selective focusing in inhomogeneous fields (see Chapter 11) is not applicable because electrostatic forces on the particles in these fields are dominated by the molecular charge.

As it turns out, the most practical, if not the only possible, way to state select ions starts with a neutral parent molecule that is photoionized. Supersonic expansion can provide a high density of molecules in low-lying levels. The cross section for photoionization is typically several orders of magnitude smaller than that for resonance excitation. Fortunately, the ease of detection of ions or subsequent ionic reaction products compensates that disadvantage to some extent.

There are three distinctively different pathways to vibrationally selected molecular ions reported in the literature: (1) single-photon ionization out of the molecular ground state, (2) resonantly enhanced multiphoton ionization, and (3) a somewhat more indirect but versatile photoelectron–ion coincidence technique.

#### 12.3.3.2 Vibrational Autoionization

The possibility of creating vibrationally state-selected ions by single-photon ionization was realized as early as 1968 by Chupka et al. (1968). This technique relies on a favorable overlap of the electronic wave functions involved. A most favorable case is the \( \text{H}_2 \) molecule, because its photoionization is dominated by very strong vibrational autoionization with little direction ionization. Vibrational autoionization of alkali molecules has been studied in beams by Leutwyler, Hofmann, Härr, and Schumacher (1981) and Eisel et al. (1983), among others. The first study of reactions with vibrationally selected ions (\( \text{H}_2 (v) + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \)) is the work of Chupka et al. (1968). More recently, Anderson, Houle, Gerlich, and Lee (1981) investigated the same reaction using more advanced experimental techniques. \( \text{H}_3^+ \) ions in various vibrational levels are formed by photoionization of a \( \text{H}_2 \) molecular beam with an appropriate UV wavelength. They are guided by multipole RF fields to the reaction chamber. The reaction products are mass analyzed and
transferred to the detector by a quadrupole filter. The experimental setup is rather complex but does allow a very efficient and clean production of $\text{H}_2(\nu)$ and detection of products. The realization of a high collection efficiency also eliminates the most serious source of dynamical bias in product detection that is common in this type of experiment.

12.3.3.3 Coincidence Techniques. Photoionization allows control of the maximum internal energy of the ion. When the internal energy of the parent molecule and the energy of the photoelectron are known, in addition to the photon energy, the internal energy of the molecular ion can be established by energy balancing. Thus, if the product molecule of an ion--molecule reaction is measured in coincidence with a photoelectron ejected from the reagent ion, the internal energy of the latter is known for this particular event. Tanaka and Koyano (1978), Koyano and Tanaka (1980), and Honma, Kato, Tanaka, and Koyano (1984) as well as Weiss, Hsieh, and Meisels (1979) detected zero kinetic energy electrons to study various ion--molecule reactions or fragmentations of SO$_2$ prepared in selected vibrational levels. The threshold photoelectrons and photoions are extracted from the ionization zone in opposite directions. Using threshold electrons as an indicator of the formation of an ion with a well-defined internal energy has the advantage that the detection efficiency is independent of the ion's vibrational level. The wavelength of the light source must be changed to vary the vibrational energy of the ion.

A modified approach using fixed-frequency photoionization, but detecting finite-energy photoelectrons in coincidence with reaction products, has been described by van Pijkeren, van Eck, and Niehaus (1983, 1985) and van Pijkeren, Boltes, van Eck, and Niehaus (1984). They measure coincidence and uncorrelated spectra as the transmission energy of the electron energy analyzer is scanned. Dynamical bias in the detection process (angular or energy discrimination in detecting the electron) is eliminated to some extent by using carefully designed collection optics and appropriate normalization procedures.

12.3.3.4 Resonantly Enhanced Multiphoton Ionization. A greater flexibility in the selection of the molecular ions vibrational state, compared with single-photon vibrational autoionization, is gained by resonant multiphoton ionization (Glownia, Riley, Colson, Miller, and Compton 1982; Achiba, Sato, Shobatake, and Kimura 1983; Pratt et al. 1984a, 1984b; Conaway et al. 1985). A specific vibrational level of an electronic state is excited by a resonant one-, two-, or three-photon transition. The subsequent ionization by an additional photon from the same laser (Fig. 12.22) generally does not involve autoionizing resonances. Because of insufficient photon energy of readily available tunable laser sources, 1 + 1 photoionization is promising at this time for only a small number of molecules with low ionization potential (e.g., alkali dimers). The feasibility of such processes, however, has been demonstrated for several molecules, including NO (Wilson, Viswanathan, Sekreta, and Reilly 1984; Dixit, Lynch, McKoy, and Huo 1985). The cross section for resonant three-photon excitation is typically several orders of magnitude smaller than the corresponding two-photon process. Therefore, the 2 + 1 scheme seems to be the most versatile and efficient one.

Figure 12.22 Multiphoton ionization using a 3 + 1 (a), 2 + 1 (b), and 1 + 1 (c) excitation scheme. The photon kinetic energy increases from a to c.
The vibrational level of the Rydberg state determines the vibrational level of the resulting ion, if the resonant intermediate state and the ion have a similar geometry. Then a strong propensity for the preservation of the nuclear motion is observed in the ionization process. This is true not only for diatomics, such as \( \text{N}_2 \) (Pratt et al. 1984a), but also for polyatomic molecules such as \( \text{NH}_3 \) (Giovanis, Riley, Colson, and Nieman 1980a, and 1980b; Conaway et al. 1985). Figure 12.23 shows photoelectron kinetic energy spectra from a \( 2+1 \) ionization of \( \text{NH}_3 \) by means of various vibrational levels of the \( \tilde{B} \) state. The wavelength of about 300 nm is obtained from a frequency-doubled Nd\(^{3+}\):YAG-pumped dye laser. The dye laser photon energy is given at the horizontal scale. The isolated peak indicates the predominant formation of the ions in a particular vibrational level, which can be identified from energy conservation. Here, the ionization process is governed by the corresponding Franck–Condon factors; typically more than 80% of the ions are produced in a \( \Delta \nu = 0 \) process from the excited state of the neutral molecules. Pratt et al. (1984b) point out, however, that one cannot generally rely on the Franck–Condon principle to predict accurately vibrational branching ratios following resonant multiphoton ionization. Figure 12.24 gives, as an example, the photoelectron kinetic energy spectrum of \( \text{H}_2 \) ionized in a \( 3+1 \) process by means of the \( C^1\Pi_u \) state. Although Franck–Condon factors predict a small decrease in selectivity with increasing \( \nu \), the extent to which it is actually observed is much larger. It is determined by more subtle details of the dynamics of the ionization process.

The extent to which the ionization out of a Rydberg state can be uncoupled from the interaction with the ion core was demonstrated recently by Pratt et al. (1984a). They showed that even electronic excitation of the core may survive the ionization process, leading to vibrationally selected and electronically excited ions. Similar uncoupling of the ionic core was observed previously in the photoionization of \( \text{Ne}^{(3}\Sigma_g^+) \) by Ganz, Lewandowski, Siegel, Bussert, Waibel, Ruf, and Hotop (1982) and Siegel et al. (1983). They found atomic ions in well-defined polarized fine-structure states, which are predetermined by the intermediate level (see also Bussert and Klar 1983).

12.3.3.5 Polarization Effects. Laser photoionization involves interaction with polarized light. One must therefore expect the resulting photoions to be aligned. Although the alignment of photions has been verified in several cases (e.g., Rothe, Ranjbar, Sinha, and Reck 1981; Poliakoff, Dehmer, Dill, Parr, Jackson, and Zare 1981; Booth, Bragg, and Hancock 1985), collision experiments with aligned ions are scarce. Rothe, Ranjbar, and Sinha (1981) studied the orientational effect on the collision-induced dissociation of \( \text{Na}_2^+ \) molecules aligned by two-step \( 1+1 \) photoionization.

As a prerequisite to collision experiments, the degree of alignment of the reagent ion should be experimentally established. Unfortunately, this may not always be easy to do because of the lack of sufficiently detailed spectroscopic information. Also, another laser will be required for laser-induced fluorescence analysis (see Chapter 9, section 9.1.5). The degree of alignment is generally difficult to predict because it depends on the number of
photons involved, the actual excitation kinetics, and the degree of saturation in the process.

When ions can be extracted from an expansion at a sufficiently high density and low temperature, the selection principles of section 12.2 are applicable, at least in principle. Electron impact forms ions typically at elevated rotational temperatures (see, e.g., Allison, Kondow, and Zare 1979; Helvajian, Dekoven, and Baronavski 1984), and subsequent expansion cooling is advisable (Johnson, Alexander, Hertel, and Lineberger 1984). Alternatively, the ions can be formed by Penning ionization in the stagnation region, with a subsequent carrier-gas-driven expansion (Guyer, Hüwel, and Leone 1983).

12.4 State Preparation by Selective Population or Depletion of Atomic Ground and Electronically Excited States

Application of molecular state selection is still in its infancy compared with experiments with state-selected atoms. The reasons for this are obvious. Because of the less favorable partition function, the population of individual molecular levels is significantly smaller, the level-to-level transition probability is typically smaller, and the number of degenerate $m$ levels is typically much larger. Thus, the requirements concerning laser power and degree of laser polarization are less demanding in the case of atoms. The basic concepts of state selection including preparation of alignment, however, are the same for atoms and molecules. Most of the results of the subsequent discussion of state selection in electronically excited atomic states also apply to molecules.

Polarization of the atoms in a collision experiment allows the selection of states with specific angular momentum, $\Omega$, along the axis of the quasi-molecule at larger internuclear distance. One of the fundamental questions to be answered in this and similar collision problems is to what extent the component $\Omega$ is conserved in the course of the collision (see, e.g., Reiland, Jamieson, Tittes, and Hertel 1982; Hertel, Schmidt Bähring, and Meyer 1985). There are two extreme cases. If the asymptotically prepared $\Omega$ remains a good quantum number—that is, if the axis of symmetry of the electron cloud remains locked onto the internuclear axis—the process develops along a single adiabatic potential energy curve. If, on the other hand, the electron cloud does not remain locked during the course of the collision, $\Omega$ is no longer well defined and mixing between adiabatic curves occurs. In reality, the internuclear distance at which the electron cloud locks onto the internuclear axis is determined by the collision system. Strong coupling to the axis results in a large locking radius; weak coupling leads to a small one.

The number of publications dealing with the technique and application of atomic state selection to collision problems is enormous and reference can be made only to a very small fraction. Most, but not all, of the work has been done on the ground state of alkali atoms and atoms of similar electronic structure, namely, the metastable states of rare gas atoms. The selection principles are similar in both cases. When only the total level population is of interest, the calculation of the equilibrium or time-integrated population is straightforward using the two-level or three-level

---

**Figure 12.24** Photoelectron spectra of H$_2$ following 3 + 1 ionization by means of $v' = 0$ to 4 of the $c^4\Pi_u$ state. [Reproduced from Pratt et al. (1984b), with permission.]
excitation scheme. In beam experiments, however, the polarization characteristics invariably need to be considered because (a) unlike most cell experiments, spherical symmetry in the approach channel of the collision system is not ensured, (b) excitations with polarized light will lead, with only few exceptions (see section 12.4.1), to polarized excited states, and (c) in most cases optical pumping effects, the consequences of which are not always intuitively obvious, will be important. Thus, the focal point will be the polarization of levels. Three different approaches can be distinguished:

1. Redistribution of the population of degenerate $m$ levels by successive optical pumping cycles on a quasi two-level system induced by polarized light.

2. Selective depletion of a particular subgroup of degenerate $m$ levels by pumping on a quasi three-level system.

3. Selective depletion of the population of an individual $m$ level by optical pumping on a quasi three-level system in a magnetic field that removes the $m$-level degeneracy.

The knowledge of the role of electronic excitation in inelastic and reactive processes is far from complete. Thus, selective population and alignment of short-lived atomic states are also of interest. High-lying states can be reached by two-step excitation starting from the electronic ground state or an excited metastable state.

The number density of particles that can be prepared in short-lived states is small, and scattering experiments are more difficult (see Chapter 26). Also, the radiative decay of the populated levels adds another component to the excitation kinetics of these levels. In contrast to a two-level system, there is no stationary population in the excited state. The time the atoms spend in the excited level is of the order of the natural lifetime $\tau$. For dipole-allowed transitions, $\tau$ is of the order of 10 ns, which is 2 orders of magnitude smaller than the typical flight time through a laser beam or collision region. As a consequence, the number of excited atoms in the scattering region is much smaller. Although alternative techniques for the state-selective preparation of rare gas fine structure states, for example, have been developed (e.g., Golde and Poletti 1981; Golde and Ho 1985), optical techniques are dealt with exclusively in the following.

12.4.1 Analytical Solution of the Rate Equations

The measurement of relative cross sections for different initial $m$ levels in short-lived states requires knowledge of the time-integrated populations. Analytical solutions of the rate equations without $m$-uncoupling approximations are given by Busseri (1986) in the limit of large excitation probabilities ($E \to 1$). Specific results are presented for $j_i = 0 \to j_f = 1$, and $j_i = 2 \to j_f = 3, 2, 1$ transitions. These are the pumping schemes applied to polarize the most popular atoms such as sodium or calcium in their electronic ground states and the rare gases in their metastable states $^3P_0$ and $^3P_2$.

The excitation rate depends on the $m$ quantum number, thus the population distribution over the $m$ levels of both the $j_i$ level and the $j_f$ level varies with time. It is the time integrated population, however, that matters in collision experiments, as long as the residence time $\tau_{\text{eq}}$ in the upper state is short compared with
the interaction time, \( t_r \), with the pump laser or residence time in the collision region. Bussert (1986) observes that the time-integrated population in a system of three nondegenerate levels is readily obtained without using the analytical solution of the rate equations that read

\[
\dot{N}_1(t) = \delta A_2 N_2(t) + W_{21}(N_2(t) - N_1(t)) \tag{12.29a}
\]

\[
\dot{N}_2(t) = -A_2 N_1(t) - W_{12}(N_2(t) - N_1(t)) \tag{12.29b}
\]

\[
\dot{N}_3(t) = (1 - \delta)A_2 N_2(t) \tag{12.29c}
\]

where \( \delta = A_{21}/A_2 \) is the branching ratio for spontaneous decay and \( N_i(t) = n_i(t)/\sum_n n_n(t) \) is the relative population in level \( i \). Thus, with \( \delta = 1 \), equation (12.29) describes a pure two-level system. Integration of the sum of equations (12.29a) and (12.29b) yields

\[
[N_1(t) + N_2(t)]_0^\infty = -(1 - \delta)A_2 S \tag{12.30}
\]

with

\[
S = \int_0^\infty N_2(t) \, dt \tag{12.31}
\]

At \( t = 0 \), \( N_1(0) = 1 \). In the limit of an excitation probability, \( E \to 1 \), \( N_i(\infty) = N_2(\infty) = 0 \) is valid because the initial population of level 1 has been completely transferred to level 3. Thus, we obtain from equations (12.31) and (12.30) with \( A_2^{-1} = \tau \)

\[
S = \frac{1}{1 - \delta} \tau \tag{12.32}
\]

Although the speed of transfer from level 1 to 3 depends on the excitation rate \( W_{12} \), the time-integrated relative population is independent of \( W_{12} \). S of equation (12.31) is an effective residence time in level 2 that differs from the natural lifetime, \( \tau \), by an efficiency factor \( \eta > 1 \) given by

\[
\eta^{n_d} = \frac{1}{1 - \delta} \tag{12.33}
\]

for nondegenerate levels.

For \( \delta \to 1 \), these and the following results are invalid because, in a quasi two-level system, \( r_{n_b} > r_t \) may be found and the asymptotic solution does not apply.

Of interest here are systems of degenerate levels, for which equations (12.29a) through (12.29c) are more complex

\[
\dot{N}_1(m, t) = \delta A_2 \sum q c_{q,m} N_2(m + q, t)
\]

\[
+ W_{21} c_{q-1,m} S (N_2(m + q_0, t) - N_1(m, t)) \tag{12.34}
\]

\[
\dot{N}_2(m, t) = -A_2 N_1(m, t) - W_{12} c_{m-1,q} S (N_2(m, 1) - N_1(m - q_0, t))
\]

\[
\dot{N}_3(m, t) = (1 - \delta)A_2 \sum_{m} N_2(m, t)
\]

The square of the Clebsch–Gordan coefficient \( c_{m} = (1, q, j, m \mid j, m + q)^2 \) describes the variation of the transition probability with \( m \). The sum runs over \( q = \pm 1 \) and 0 according to the three transitions \( \Delta m = \pm 1, 0 \) of the spontaneous decay of \( m \) states of level 2. For excitation with linear or circular \( \sigma^- \)-polarized light \( q^0 \) takes the value 0 or 1. Integration of the sum

\[
N_1(m, t) + N_2(m + q_0, t) \quad \text{with} \quad N_2(m, 0) = N_2(m, \infty) = 0 \quad \text{leads to}
\]

\[
N_1(m, \infty) - N_1(m, 0) = A_2 \sum_{q} \left( c_{q,m} \delta - \delta_{q,0} \right) S_{m+q} \tag{12.35}
\]
The number of unknown quantities \( S_m, m = 0 \) and \( N_i(m, \infty) \) is equal to the number of equations, as can be verified from Fig. 12.25, which gives the relative magnitude of the level-to-level transition rate. Depending on the particular excitation scheme, some levels in state 1 are not depleted but populated by spontaneous fluorescence, and some levels in state 2 are not populated. For the latter, \( S_m = 0 \) at all times and \( N_i(m, \infty) = 0 \) for all levels that have a nonvanishing excitation probability. As an example, consider \( j_i = 2 \rightarrow j_f = 2 \). Excitation with linearly polarized light depletes the population of \( N_i(m) \) with \( m = 1 \) and 2, while \( N_f(m = 0) \) remains unpopulated. Thus, it follows that \( S_0(0) = 0 \) and \( N_i(m) = 0 \) for \( m = \pm 1, \pm 2 \). The five equations are sufficient to determine \( S_i(m) \) with \( m = \pm 1, \pm 2 \) and \( N_i(0) \).

Similarly, the unknown quantities are \( S(m) \) for \( m = 1, 0, +2, +2 \), and \( N_i(2) \) when excitation occurs with \( \sigma^+ \) light, since \( S(-2) = 0 \) and \( N_i(2) = 0 \) for \( m = -2, 1, 0 \).

The linear equation (12.35) is independent of the excitation rate, since only the solution in the limit of saturation is sought. The polarization of the levels can be described by state multipoles \( T_{10} \) (see, e.g., Blum 1978; Fischer and Hertel 1982)

\[
T_{10} = \sum_{m} (-1)^{j_i + m}(j_f, m, j_f, -m | k0)S_i(m) 
\]

The ratio

\[
M_r = \frac{T_{10}}{T_{00}}
\]

specifies the population distribution uniquely. They can be determined from equations (12.35) and (12.37) for arbitrary population distributions \( N(m, 0) \) of the initial level. The results for isotropic initial population in level 1 are given for various excitation schemes in Table 12.3.

These results are particularly noteworthy. For \( j_i = 0 \rightarrow j_f = 1 \) excitation, only one level \( (j_f, m) \) is populated. Therefore, the multipoles are independent of the branching ratio \( \delta \). The most surprising result is the fact that *isotropic* time-integrated population is found for \( j_i = 2 \rightarrow j_f = 1 \) transitions for excitation with both linear and circular polarized light. This seems to be counterintuitive. For excitation with linearly polarized light the level \( (j_f, 0) \) is populated more strongly than \( (j_f, \pm 1) \) in the initial phase of the pump cycle because the \( (j_i, 0) \rightarrow (j_f, 0) \) excitation probability is largest. The level \( (j_f, 0) \) is therefore more rapidly depleted than \( (j_f, \pm 1) \). As a result, in the final phase \( (j_f, \pm 1) \) has higher population than \( (j_f, 0) \). As it turns out, the number of molecules that are transferred to level 3 through the levels \( (j_f, m_f) \) is the same for all \( m_f \) values. Thus, the time-integrated multipoles are zero.

The multipoles depend on the branching ratios for \( j_i = 2 \rightarrow j_f = 2 \) excitation with linear and circular polarized light. The multipoles of \( j_i = 3 \) are given in Table 12.3 only for the special case \( \delta = 1 \). This corresponds to a two-level system, with \( \text{Na}(3s, F = 2) \rightarrow \text{Na}(3p, F = 3) \) being a well-known example.
The ground state $j_i = 2$ multipoles prepared by population redistribution are $M_2 = -0.797$ and $M_4 = 0.267$ for $\pi$ pumping but $M_1 = 0.070$, $M_3 = 0.598$, $M_2 = \pm 0.707$, and $M_4 = 0.267$ for $\sigma^*$ pumping. In the case of $\pi$ or $\sigma^*$ pumping of $j_i = 2 \rightarrow j_f = 2$, only the ground state levels $(2, 0)$ or $(2, \pm 2)$, respectively, remain populated. Although the time-integrated $j_f = 1$ multipoles induced by $j_i = 2 \rightarrow j_f = 1$, $\pi$ or $\sigma$ pumping are zero, the corresponding initial state multipoles are nonvanishing. It is interesting to determine the state multipoles for excitation with unpolarized light that can be described as an incoherent superposition of $\sigma^+$ and $\sigma^-$ light of equal intensity. In this case, the last term of equation (12.35) is given by the sum for $q_0 = +1$ and $q_0 = -1$. The results are given in Table 12.4. In contrast to excitation with polarized light, the competition between the $\sigma^+$ and $\sigma^-$ excitation paths leads to a nonvanishing moment $M_2$ for $j_i = 2 \rightarrow j_f = 1$ pumping and a dependence of the multipoles for the two-level pumping scheme on the excitation rate $W_{12}$.

12.4.2 Experiments Involving Atomic Ground States
Beam experiments with atomic ground state polarization are a direct application of the original idea of Kastler (1950). The theory of optical pumping, with emphasis on the application to atoms, has been reviewed by Happer (1972). In the following, only a few aspects considered in recent beam work are discussed. Most of the work has been done with alkali atoms. In contrast to other selection techniques, such as selective deflection in inhomogeneous fields, laser optical pumping achieves polarization by redistribution of $m$-level population and thus does not result in a loss of total beam intensity (see, e.g., Hils, Jitschin, and Kleinpoppen 1981). Pumping with circularly polarized $\sigma^+$ or $\sigma^-$ light on a two-level system enriches the population in the level $m = +j$ or $m = -j$, respectively. Complete ground state polarization can be achieved by pumping on a two-level system, such as

<table>
<thead>
<tr>
<th>$j_i$</th>
<th>$j_f$</th>
<th>Polarization</th>
<th>$M_1$</th>
<th>$M_2$</th>
<th>$M_3$</th>
<th>$M_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$\pi$</td>
<td>0</td>
<td>-1.414</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma^*$</td>
<td>$\pm 1.225$</td>
<td>+0.707</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\pi$</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma^*$</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2$^a$</td>
<td>$\pi$</td>
<td>0</td>
<td>$1.195 \frac{3 + 2\delta}{12 - \delta}$</td>
<td>0</td>
<td>$- 2.405 \frac{2 - \delta}{12 - \delta}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma^*$</td>
<td>$\pm 4.243 \frac{6 + \delta}{N}$</td>
<td>$-3.586 \frac{6 - 5\delta}{N}$</td>
<td>$\pm 0.707(18 - 27\delta + 10\delta^2)/N$</td>
<td>$-0.802 \frac{6 - 5\delta}{N}$</td>
</tr>
<tr>
<td>2</td>
<td>3$^c$</td>
<td>$\pi$</td>
<td>0</td>
<td>-0.962</td>
<td>0</td>
<td>0.640</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma^*$</td>
<td>$\pm 1.5$</td>
<td>1.443</td>
<td>1.080</td>
<td>0.640</td>
</tr>
</tbody>
</table>

*From Bussert (1986), reproduced with permission.

$^a$ $N = 72 - 30\delta + 5\delta^2$, $\delta = A_{21}/A_2$.

$^b$ For $\delta = 1$. The higher multipoles are $M_3 = 0$, $M_4 = -0.232$ for $\pi$ excitation and $M_3 = \pm 0.289$, $M_4 = +0.087$ for $\sigma^*$ excitation.
<table>
<thead>
<tr>
<th>$j_i$</th>
<th>$j_f$</th>
<th>Multipoles of Level $j_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$M_2 = +0.707$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$M_2 = -1.4142(10 - 3\delta)$</td>
</tr>
<tr>
<td>2</td>
<td>2*</td>
<td>$M_2 = \frac{-1.195(57 - 32\delta + 15\epsilon)}{N_2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$M_4 = \frac{16.036(2 - \delta - 2\epsilon)}{N_2}$</td>
</tr>
<tr>
<td>2</td>
<td>3*</td>
<td>$M_2 = \frac{0.577(2058 + 870\epsilon + 12\epsilon^2)}{N_3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$M_4 = \frac{0.213(-3540 + 792\epsilon + 48\epsilon^2)}{N_3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$M_6 = \frac{0.174(672 + 528\epsilon + 96\epsilon^2)}{N_3}$</td>
</tr>
</tbody>
</table>

* $N_2 = 5[(30 - 17\delta) + (18 - 70)\epsilon]$.  
* $N_3 = (1316 + 1084\epsilon + 248\epsilon^2)$.  


The Na($3^2S_{1/2}, F = 2 \rightarrow 3^2P_{3/2}, f = 3$) level. However, the hyperfine splitting of the ground state level (1772 MHz for sodium and 228 MHz for lithium) prevents the participation of all atoms in the pump process, and a fraction of the atoms remains unpolarized unless a Stern Gerlach magnet is used to deflect $F = 1$ atoms (Dreves, Kamke, Broer, and Fick 1981). Another possibility is to use one laser beam that intersects the molecular beam at 90° and under an appropriate angle $\theta < 90°$ to Doppler-shift the absorption frequency. This arrangement leads to the polarization of only a subgroup of molecules within a narrow range of velocities (see also section 12.2.4). Also, a polarized broadband source could be used to pump both levels simultaneously, but the spectral energy density of those sources is too small for effective pumping. Baum, Caldwell, and Schröder (1980) used an acoustooptical modulator to frequency-shift part of the laser beam by 228 MHz. Thus, crossing the atomic beam at right angles with the two superimposed laser beams results in a complete polarization of the atoms that accumulate in the $m_F = +F_{\text{max}}$ or $m_F = -F_{\text{max}}$ level of the ground state. Another technique to achieve complete polarization has been proposed by Dreves, Jänsch, Koch, and Fick (1983). They use an RF field of 1772 MHz to transfer population of the $F = 1$ state to the $F = 2$ state of sodium while laser pumping the transition $F = 2 \left( ^2S_{1/2} \right) \leftrightarrow F = 3\left( ^2P_{3/2} \right)$ with $\sigma^+$ light to drive atoms into the $F = 2$, $m_F = \pm 2$ ground state level. Subsequent adiabatic high-frequency transitions (Haebt'77) induced in a magnetic field of intermediate strength to remove the $m$-level degeneracy allows the transfer of population into any of the $m_F$ levels. The polarization can be detected by the standard laser-induced fluorescence technique (see Chapter 9, section 9.1.5). Alternatively, the degeneracy of $m_F$ levels can be removed by a magnetic
field. This approach allows the determination of the population of each individual level (Cusma and Anderson 1983; Dreves et al. 1983) and does not require the analysis of fluorescence polarization. However, the characteristics of the anisotropic emission must be taken into account when computing relative $m_r$ level populations from relative fluorescence intensities (see Chapter 9, section 9.1.1).

12.4.3 *Experiments Involving Electronically Excited States*

Although a technique for selective quenching of the population of individual fine-structure states of metastable atoms using conventional light sources has been demonstrated (Golde and Poletti 1981; Golde and Ho 1985), most of the state-selected molecular beam work has been done with lasers. Because of convenient production and detection, metastable states of rare gas atoms, in particular, have been studied. Unfortunately, the beam emerging from an electric discharge or electron impact source contains atoms in more than one metastable state. An early example of optical state selection is the work of Fry and Williams (1969) as well as Hotop, Niehaus, and Schmeltekopf (1969), who used a discharge lamp to depopulate the metastable $2^3S_1$ state of helium but leaving the population in the $2^3S_1$ state unchanged. A helium discharge lamp emits light of sufficient intensity on the $2^3P\rightarrow 2^1S_0$ transition to excite all atoms in the $2^3S_0$ state to the $2^3P_1$ level from which they radiate to the $1^1S_0$ electronic ground state. An extension of that technique, including polarization of the $^1S_0$ state by optical pumping with an incoherent light source is described by Riddle, Onellion, Dunning, and Walters (1981). Photons from an RF-excited flowing helium lamp interact with the beam particles downstream of the interaction region with another helium lamp that depletes the $2^3S$ level. The discharge tube of the latter spirals around the beam axis. The radiation of the former lamp is filtered to select the 1.08-µm radiation for $2^3S\rightarrow 2^3P$ excitation. Circular polarization ensures accumulation of atoms in the $m_r = 1$ state of the $2^3S$ level. Subsequent analysis of the beam with a Stern-Gerlach magnet showed a high degree of polarization. This state-selection scheme has also been applied to study the polarization dependence of the secondary electron yield from surfaces (Onellion, Hart, Dunning, and Walters 1984). Selective quenching by optical pumping with a color center laser is another possibility (Giberson, Cheng, Onellion, Dunning, and Walters 1982).

An early example of polarization of the metastable ($^3P_r$) state of neon is the work of Scheerer (1969a), who also studied depolarization cross sections of optically oriented rare gas atoms (Scheerer 1969b) in the bulk.

Ionizing collisions of neon atoms in the metastable $^3P_r$ state ($3s$ in Paschen notation) as well as in the higher-lying levels with total angular momentum $J = 1$, 2, and 3 ($2p_1$, $2p_2$, and $2p_3$, respectively, in Paschen notation, in LS-coupling the $2p_3$ level is labeled $^3D_3$) have been studied extensively (Bussert, Bregel, Ganz, Harth, Siegel, Ruf, Hotop, and Morgen 1985). Of particular interest is the $^3D_3$ level since spontaneous electric dipole decay always leads back to the pumped $^3P_2$ state and the pump-decay cycle is confined to a quasi two-level system. A laser beam of typically 150 mW and a diameter of 4 mm allows about 250 spontaneous emission processes. In fact, it has been shown
from the angular distribution of photoelectrons, ionized out of the $^2D_3$ state, that the polarization of this level is very close to the theoretical limit (Fig. 12.26) for saturated pumping (Siegel et al. 1983). The two-level nature of the $^3P_2 \rightarrow D_1$ pump cycle allows the buildup of a substantial population in the upper level, when excitation occurs with a CW laser. Because of saturation broadening (Bussert, Bregel, Allan, Ruf, and Hotop 1985), the transition line width given by $\gamma_{\text{sat}} = \gamma_l (1 + (I/I_{\text{sat}}))^{1/2}$ with $I_{\text{sat}} = f\pi^2\gamma_l h c / 3 \lambda^2$ and $f = 1$ for $^1S$ light or $f = 1.83$ for linearly polarized light (Hertel and Stoll 1977; Fischer and Hertel 1982) is broader than the Doppler width resulting from the divergence of the atomic beam. Thus, all atoms, irrespective of their transversal velocity component, can be pumped. The efficiency of the pump process may be reduced if elastic scattering from the target gas leads to larger transversal velocity distributions in the interaction region.

In these experiments, ionization processes resulting from the polarized $^3D_3$ and $^3P_2$ levels can be separated by virtue of an energy analysis of ejected electrons. For neon–argon collisions, Bussert, Bregel, Allan, Ruf, and Hotop (1985) and Bregel, Bussert, Ganz, Hotop, and Ruf (1986) found only a comparatively weak polarization dependence for processes involving the $^3P_2$ level but a strong dependence on the level polarization for the $^3D_3$ state.

Studying collision processes out of higher-lying states with total angular momentum $J = 1$ and 2 is significantly more difficult. These levels decay to nonpumped states. Therefore, the “effective residence time,” $\tau_{\text{eff}}$ (see section 12.4.1), is comparable to the
natural lifetime of only 20 ns, and a loss of signal of 2 orders of magnitude results. The consequences for the experimental setup are mentioned in section 12.4.5.

An alternative technique of metastable level polarization has been demonstrated by Bender, Beyer, Haberland, Hausmann, and Ludescher (1985). They remove the degeneracy of the \( m \) levels by Zeeman splitting in a homogeneous magnetic field (Fig. 12.27). Excitation with a single-mode laser allows the depletion of a particular Zeeman state. Downstream of the excitation zone, the atoms pass through the fringing magnetic field of a small rotatable horseshoe magnet. Because of their low velocity, the \( m \) labeling of their quantum state is conserved with respect to the new local field direction. The Zeeman splitting of the levels is too small to affect the collision dynamics. Taking the difference of the scattering signal with and without laser pumping allows the isolation of the contribution of one \( m \) state, the quantization axis of which is continuously variable. In another experiment the same group (Haberland, Huber, and Karras 1987) scattered the \( m \)-selected beam from atoms in their ground state and used a third magnet and second laser to detect atoms in an \( m \) level. In this way a complete set of \( m \rightarrow m' \) differential cross sections has been obtained.

Calcium atoms in the metastable states \( ^3P_2 \) and \( ^1D \) states can also be conveniently produced. Telle and Brinkmann (1980) measured the reaction cross sections with Cl and HCl for the chemiluminescent channel. Refined collision experiments including laser state selection with the \( ^3P_2 \) manifold have recently been conducted by Yuj and Dagdigian (1983a, 1983b) for intramultiplet

Figure 12.27  Total Ne* intensity as a function of laser detuning. A depletion of the \( ^3P_2 \) level population with five \( m \) states of the order of 10% is observed as the laser is tuned across the Zeeman pattern. The population depletion of individual \( m \) levels is of the order of 50%. [Reproduced from Bender et al. (1985), with permission.]
mixing and by Yuh and Dagdigian (1984) for the chemical reaction. They deplete the population of a particular fine structure level by pumping on the \( \text{He}^1S \rightarrow \text{He}^5P \) transition near 610 nm. The population of the pumped level is redistributed among the other fine structure states by spontaneous decay from the \( \text{He}^5S \) level. A laser beam of 50 mW and diameter of 4 mm was sufficient to reduce the population of a given level to less than 5% of its original level. Yuh and Dagdigian (1983a, 1983b) emphasize the importance of understanding the pumping cycle quantitatively. In particular, the possibility of creating coherence in the pumped level needs to be considered, because coherence would complicate the interpretation of the data. They conclude that no coherences are present in their optical pumping experiments, partly because of mixing in the earth’s magnetic field and efficient averaging because of the spread in beam velocity. The optical pumping occurs upstream of the scattering region. An alignment procedure to ensure the detection of the chemiluminescence from those atoms that are optically pumped is discussed in section 12.4.5.

Molecular beam scattering experiments involving electronically excited, and in most cases aligned or oriented, atoms have been performed since 1975. They include the study of total differential scattering (e.g., Carter, Pritchard, Kaplan, and Ducas 1975; Düren, Hasselbrink, and Illrichs 1984), electronic to vibrational energy transfer (Hertel, Hofmann, and Rost 1976; Hertel 1982), chemical reactions (Rettner and Zare 1981, 1982) and associative ionization in \( \text{He}^1S + \text{He}^5P \) collisions (Runge, Pezelle, Perdix, and Watel 1985) or \( \text{Na}^3p + \text{Na}^3p \) collisions (Kircz, Morgenstern, and Nienhuis 1982). Most of the related experiments as well as the techniques to prepare a sufficiently high population in the excited state are discussed in Chapter 26, and are therefore not discussed in further detail here.

12.4.4 Two-Step Excitation of Higher-Lying Levels

The effect of electronic excitation of reactant atoms on reactive scattering is often quite dramatic. The role of characteristic properties of charge distribution, such as size and orientation, in reaction dynamics is far from being fully understood. The results of only a few collision experiments in beams involving highly excited atoms have been published so far. Jamieson, Reiland, Schulz, Tittes, and Hertel (1984) studied the quenching of \( \text{Na}^* \) \((4D, 5S, 4P, 4S)\) by \( \text{N}_2 \), Schmidt, Weiss, Mestdagh, Covinsky, and Lee (1985) investigated chemical reactions of higher-lying \( \text{Na}^* \) levels with \( \text{O}_2 \), and Bregel et al. (1986) studied ionizing collision of excited neon atoms. Vernon, Schmidt, Weiss, Covinsky, and Lee (1986), also reported results for reactions with HCl and Cl\(_2\). The surprising result is that reactions with Cl\(_2\) showed little dependence on electronic excitation, although excitation effectively lowered the ionization potential of sodium by more than 2 eV. The \( \text{Na}^* + \text{HCl} \) reaction shows significantly different translation energy distributions and polarization characteristics for the various entrance channels. The most surprising result, however, is that the \( \text{Na}^* + \text{O}_2 \) reaction to form NaO is observed only for the Na\((4D)\) state, although lower-lying electronically excited states are sufficiently energetic to overcome the endothermcity of about 2 eV of the reaction.

The main experimental obstacle in the study of processes involving short-lived states—the short effective residence time in
the excited level—has been already mentioned (section 12.4.3). In most cases, two lasers are needed to reach the desired level. To some extent pumping on a sequence of quasi two-level systems can enhance the population in excited states. For example, optical pumping of the \(4^2D_{5/2} \) level of sodium is best accomplished by using circularly polarized \( \sigma^+ \) light for both lasers (Fig. 12.28). In the first excitation step, all atoms in the collision center are pumped in the \(3^2S_{1/2} \) \((F' = 2, m_F = 2) \rightarrow 3^2P_{3/2} \) \((F = 3, m_F = 3)\) two-level system except for those that end up in the \(3^2S_{1/2} \) \((F' = 1)\) state because of excitation processes in the wings of the line profile. In the presence of the second laser beam, atoms in the \(3^2P_{3/2} \) \((F' = 3, m_F = 3)\) level are further excited to the \(4^2D_{5/2} \) \((F = 4, m_F = 4)\) state. From there the atoms can cascade back to the \(3^2S_{1/2} \) \((F' = 2)\) state by means of the \(3P_{1/2} \) \((F = 3)\) or \(4P_{3/2} \) \((F = 3)\), \(4S_{1/2} \) \((F = 2)\), and \(3P \) path (Fig. 12.29). The \(4S \) \((F = 2) \rightarrow 3P \(F = 2, 1)\) transitions open a leak from the pumping cycle, because decay from these levels to the unpumped \(3^2S_{1/2} \) \((F = 1)\) state is possible. This leak does not prohibit establishment of a stationary population in the excited levels, because a specific group of atoms interacts only for the time \(\tau = d/v\) within the laser beam. After the time \(\tau = d/v\), they are replaced by other atoms. The ratio of the populations of the states \(4^2D_{5/2}; 4^2P_{3/2}; 4^2S_{1/2}; 3^2P_{3/2}\) has been estimated for stationary conditions to be 21:15:4:28. The ratio of the number of atoms in all the excited states to those in the \(3^2S_{1/2} \) \((F' = 2)\) level is 68:32. Jamieson et al. (1984) found that the highest population in the \(3^2S_{1/2} \) \((F = 2)\) level could be achieved by using linearly polarized light for both laser beams.

12.4.5 Experimental Problems

Effective optical pumping requires that the product of light intensity times the atom–light interaction time is large enough that many cycles of absorption followed by spontaneous emission occur (see Chapter 9, section 9.1.2). Increasing the spectral energy density also increases the rate of induced emission, which does not change the atom polarization because the system always returns to its original level. If the time the atoms spend in a light beam is much longer than the spontaneous lifetime of the excited state, the induced emission will have no net effect on the ultimate polarization that can be achieved. To prevent wastage intensity, the light should be spread out over a longer path of the beam—for example, by focusing with a cylindrical length (Baum et al. 1980) to form a slit-type focus with its long axis parallel to the beam axis. While the photon flux remains constant, the effectiveness of spontaneous processes is enhanced. The same conclusion applies, of course, to the pumping of metastable levels.

If collision processes involving a short-lived excited state that decays to other than the pumped levels are of interest, the experimental setup must be different. Optical pumping upstream of the collision region would result in an additional loss of signal because the flight time of atoms during \(t_{\text{eff}}\) in the excited level is small compared with the extension of the scattering region. Thus, focusing of the laser beam with a cylindrical lens is advisable. This arrangement ensures that a relatively large cross section of the atomic beam is pumped, but all excitation processes occur within the scattering region.

Careful matching of laser beam diameters is very important for the study of processes involving two excited particles in short-lived
states or two-step excitation. A typical flight path in the excited state is 10 \( \mu m \), and the particles may not maintain their excitation until they reach the other collision partner or the center of the second laser beam. An instructive example is given by Meijer, Meulen, and Morgenstern (1986) (see also Alkemade 1985). They study the associative ionization of two Na(3p) atoms in counterpropagating beams. One laser is used to excite atoms in both beams. If the laser intensity exceeds the saturation intensity, excitation occurs predominantly within the wings of the laser beam, and the overlap of the regions with excited atoms in the two atomic beams may be reduced significantly (see also Chapter 9, section 9.3).

Kroon, Beijerinck, Verhaar, and Versier (1984) carried out a detailed study of optical pumping of metastable Ne(\(^{2}P_{3/2}\)) atoms in a beam. They demonstrate that stray magnetic fields will normally destroy the pumping-induced polarization of the metastable levels over a distance of about 10 mm. Thus, either efficient magnetic shielding or imposing a magnetic field along the direction of laser polarization will be necessary to preserve the atomic level polarization over a longer flight path. Alternatively, precession of the angular momentum in a magnetic field perpendicular to the laser polarization leads to efficient pumping of all magnetic substates, provided the Zeeman splitting is smaller than the natural line width (see also Carter et al. 1975). Thus, the population of a metastable level can be removed completely, when excitation occurs to a short-lived state that subsequently decays to other levels.

Coherence phenomena cannot be neglected when the interaction time of the particle with the laser is of the same order of magnitude as the spontaneous lifetime of the excited state. In fact, Kroon, Senhorst, Beijerinck, Verhaar, and Verster (1985) have observed Rabi oscillations in the optical pumping of a beam of metastable neon atoms. For those atoms crossing the laser beam near the waist of the focus, an oscillatory variation of the excited state population with velocity has been found. Similar behavior was observed previously by Avrilier, Raimond, Bordé, Bassi, and Scoles (1981) for vibrational state population of SF\(^6\). Although these are very interesting phenomena, the velocity-dependent Rabi oscillations are undesirable in a collision experiment. They can easily introduce an artificial velocity dependence in the cross section under investigation.

Photons are used most efficiently for optical pumping if they are delivered to the atomic beam in a single laser mode. Multimode lasers, however, are much simpler to operate. Recently, Cusma and Anderson (1983) and Giberson, Johnson, Hart, Hammond, Jeyes, and Dunning (1984) have shown that efficient pumping and polarization can also be achieved with a multimode laser. They traded efficient use of available photons for simplicity in laser operation and found that high-power laser operation does not necessarily lead to the most efficient and stable optical pumping. Intensity fluctuations on a time scale longer than the interaction time of the atoms with the laser beams will enable groups of atoms to pass through the pumping region without being efficiently pumped. If stable laser operation is maintained in a few modes only, the overlap of the atomic absorption and laser frequency spectrum is not necessarily optimal, and tuning of the laser cavity for maximum polarization is critical. The researchers found most
efficient and stable optical pumping for laser operation conditions
that ensured stable output intensity but rapid change of the mode
structure. The mode structure can also be smeared out for stable
pumping by fast wobbling of a cavity mirror mounted on a
piezoceramic element.

A detailed description of a stable and relatively easy to use
multimode dye laser with narrow-mode spacing for intracavity
optical pumping experiments is given by Weissmann, Ganz,
Siegel, Walbel, and Hotop (1984). The same group (Bregel et al.
1986) also used an anticollinear arrangement of atomic and laser
beam for efficient and selective quenching of metastable levels.

When the transition line width is not sufficiently broad to ensure
pumping of a metastable level across the full profile of the beam, a
feedback loop, similar to the one described by Yuh and Dagdijian
(1984), should be used. If a \( ^3P_2 \) level with \( J \neq 1 \) is pumped, an
enhancement of the \( ^3P_2 \rightarrow ^1S \) emission in the scattering chamber,
monitored through the same optics used to detect the chemiluminescence,
is observed. Otherwise the monitor signal decreases.

Simultaneously, the fluorescence originating from the pump cycle
can be observed at a right angle to the pump beam through a
narrowband filter, with slits in front of the photomultiplier to
reduce the Doppler broadening. The slit position should be
adjusted until the extrema of the monitor and the laser-induced
fluorescence signal coincide. In this way, the fluorescence detector
is assured of observing that part of the \( \text{Ca}^+ \) beam that entered the
scattering chamber, since the Doppler shift for both signals is then
the same. The pump cycle fluorescence also provides a convenient
feedback signal to lock the laser frequency on a given transition.

Various techniques for polarization rotation in experiments
involving aligned species are described in Chapter 9. Instead of
the chromatic \( \lambda/2 \) plate, the approximately achromatic Fresnel
rhomb (Hecht and Zajac 1976) is often used. Rettner and Zare
(1982) point out that care should be taken to ensure a good \( \text{TEM}_{\infty} \)
mode. Azimuthal symmetry of the laser beam is particularly
important because, unlike the \( \lambda/2 \) plate, the rhomb causes the
profile of the beam to rotate. Deviation from circular symmetry
may result in a modulation of the signal as the rhomb rotates,
which is not related to polarization. Profile-related modulation,
however, occurs at only one quarter the rate of polarization vector
rotation and can thus be identified.

Identification of the scattering from excited states or back-
ground signal reduction usually requires the measurement of a
signal without excited species. Tuning the laser frequency
off-resonance rather than blocking the laser is definitely pre-
ferable, because other laser-induced processes will not change, for
example, multiphoton ionization or fluorescent light from the wall
material.

12.5 Other Selection Principles

12.5.1 Dissociation of van der Waals Molecules

Very recently, Buelow, Radhakrishnan, Catanzarite, and Wittig
(1985) demonstrated a conceptually quite attractive method to
orientate reagents. The technique involves van der Waals
molecules that have a well-defined equilibrium geometry. As a test
case, they chose the \( \text{CO}_2 \cdot \text{HBr} \) molecule formed in a pulsed
supersonic expansion to study the reaction \( \text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO} \).
The geometry of this complex is believed to be linear. The HBr molecule is dissociated with 193-nm light. Because the dissociation is direct (Zare 1972) the initial hydrogen atom velocity is directed along the HBr axis, and an H + CO₂ collision with a small-impact parameter will occur. The degree of orientation is limited by the zero-point fluctuation associated with the vibrational modes of the complex. The population of rovibronic states of OH are monitored by laser-induced fluorescence. The probe laser was collinear with the ArF photodissociating laser and intersects the molecular beam 50-nozzle diameters downstream from the orifice. The effect of the specific approach geometry is identified by comparison of the population distribution in the beam with the one obtained in a bulk mixture of CO₂ and HBr. In the bulk, no complexes are formed; thus, no restrictions on the impact parameters are imposed. As expected, the beam data show a somewhat lower rotational excitation compared with the bulk data. In this particular case, the bromine atom is moving rather slowly and may contribute to OH excitation by inelastic scattering.

The application of this technique is obviously limited to favorable cases with well-established geometry of the van der Waals complex. When applicable, however, it will provide very detailed information about the collision process.

12.5.2 "Selection" of Impact Parameters

The experimentalist is not in control of the impact parameter in a collision event. Knowledge of the impact parameter would be needed to completely specify the approach geometry and, for example, total angular momentum in a given event. The analysis of differential cross sections for inelastic events yields information about the correlation of the scattering angle and a more-or-less well-defined range of impact parameters. Such access is not available from integral cross sections for reactive processes except for particularly fortunate cases. If a reaction occurs with the exchange of a hydrogen atom by a much heavier one, such as the reaction

$$\text{Ba} + \text{HI} \rightarrow \text{BaI} + \text{H}$$

studied by Noda, McKillip, Johnson, Waldeck, and Zare (1986), the orbital angular momentum of the reaction products is small. Thus, a large fraction of the initial orbital angular momentum will be transformed into rotation of the product molecule. The population distribution over the rotational levels of the product molecules therefore, reflects the variation of reaction probability with impact parameter. The spectroscopic analysis of the BaI molecule, however, is a formidable task. Rotational levels up to \(j = 350\) are populated. From their analysis, Noda et al. (1986) concluded that a surprisingly small range of impact parameters \(2 \, \text{Å} \leq b \leq 3.2 \, \text{Å}\) contributes to reactive events forming BaI molecules in the vibrational level \(v^* = 8\).

12.5.3 Photodeflection

Photodeflection is a somewhat exotic but elegant method for atomic or molecular state selection. The transfer of the photon momentum, \(\hbar / \lambda\), associated with an absorption process, deflects a particle of mass \(m\) by an angle

$$\alpha = \frac{\hbar}{\lambda \cdot mv}$$

(12.39)
if the light beam intersects the path of the particle at a right angle. For an atomic mass $m = 20$, $v = 10^8 \text{m/s}$, and $\lambda = 600 \text{nm}$, the result is $\alpha = 3 \times 10^{-5}$ radian. A highly collimated beam is required to gain sufficient sensitivity for detection of such small deflection angles. The recoil of the subsequently emitted spontaneous photon may enhance or compensate the initial depletion, depending on the direction of emission (Fig. 12.30). Anisotropic emission following excitation with polarized light may reduce the spreading in the direction of the laser polarization, but not along the axis of the original deflection, $\Delta v$.

The phenomenon of photodeflection and spreading of a sodium beam on irradiation with sodium D-light was observed as early as 1933 by Frisch (1933). That experiment was repeated by Picqué and Vialle (1972). A number of experiments using lasers were reported shortly after that time (e.g., Schieder, Walther, and Wöste 1972; Jacquinot, Liberman, Picqué, and Pinard 1973; Nenzenzahi and Szöke 1974; Bernhardt, Duerre, Simpson, and Wood 1976). Because of the minute deflection angles, attempts have been made to repeat the absorption–emission cycle several times by pumping on a quasi two-level system (Abate 1974; Citron et al., 1977). The $^2S_{1/2}(F = 2) \rightarrow ^2P_{3/2}(F = 3)$ transition in sodium is the most prominent example. The number of absorption–emission cycles increases with the interaction time. It is ultimately limited by leakage out of the quasi two-level system because of far wing absorption of neighboring transitions. The successive absorption of, on the average, up to 75 photons by a single sodium atom has been reported (Düren, Hoppe, and Pauly 1976). So far, experiments applying photodeflection have been limited to feasibility studies in connection with spectroscopic techniques. A most impressive one is the work of Herrmann, Leutwyler, Wöstef, and Schumacher (1979), who recorded the Na$_2$ absorption spectrum by monitoring the state selective deflection out of the beam (Fig. 12.31). Assuming a trapezoidal beam profile from two collimating slits of width $d_i$ at a distance $l_i$, the relative change in signal is given by

$$\frac{\Delta I}{I} = \eta \frac{n}{n} \frac{h}{\lambda m u} \frac{l_i}{d_i}$$  \hspace{1cm} (12.40)

Here $\eta$ and $n$ are the fraction of particles that can be deflected and the number of photons absorbed per particle, respectively. For a two-level atomic system, $\eta \ll 1$ and $n \gg 1$ holds, while for a molecule $\eta \ll 1$, and $n \approx 1$ is typically valid.

It is tempting to speculate about the possible applications of state selection by photodeflection in the study of collision process of diatomic molecules. There are two extreme cases. If the Franck–Condon factor for a $v'' = 0 \rightarrow v'$ transition between the electronic ground state and an electronically excited state is small with most of the fluorescence concentrated on $v' \rightarrow v''$ transitions with $v'' \gg 1$, then the photon recoil of the spontaneous is smaller than the momentum transfer during absorption (see Fig. 12.30). The broadening associated with the deflection is less than the average deflection angle. Thus, a small cone near the beam axis will exhibit a state-selective depletion of particles. Within this small cone, the population of a single level will be depleted without population enhancement in levels $v'' > 0$. Such parasitic modulation of other levels was a major obstacle for the application of the depletion labeling technique (see section 12.2.1) to reactive
processes. If, on the other hand, the electronic transition is dominated by $\Delta v = 0$ bands, the Franck–Condon factor for the $v^r = 0 \rightarrow v^r = 0$ transition is close to unity. Several absorption–emission cycles may be possible in this case, and the average deflection angle is correspondingly enhanced. A homonuclear molecule with $Q$-branch excitation would be ideally suited. Otherwise, the $P, Q, R$ rotational branching of the fluorescence leads to the population of neighboring rotational levels, and on the average no more than two photons are absorbed. In any case, application of this technique will be limited to processes with large cross sections because the necessary high collimation of the primary beam reduces the flux to a rather low level.

12.6 Concluding Remarks
Laser state selection has revolutionized the experimental work in collision dynamics. With the techniques on hand, the experimentalist has gained nearly complete control of the molecule's internal degrees of freedom. In this chapter, state-of-the-art laser state selection has been discussed, through representative examples rather than a complete review. It is worthwhile to remember that many of the ideas of optical state selection were conceived long before the laser age. The high spectral energy of the laser

![Figure 12.31](image)

Figure 12.31 (a) Photodeflection spectrum of Na$_2$ using ($A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^-$) excitation with a multimode dye laser of 150 mW. (b) Same as part a, but with a laser power of 400 mW. Note the equalization of band-head intensities because of the onset of saturation. [Reproduced from Herrmann et al. (1979), with permission.]
radiation is, however, vital for implementation of these techniques in molecular beam experiments. Today, laser-induced fluorescence and laser optical pumping are widely used routine methods. More complex techniques such as on- and off-resonance–stimulated Raman scattering are being transferred from cell to beam experiments as well. They hold great promise for improving selectivity and flexibility of optical state selection methods.

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