Fig. 2.16a–c. Continuous "bound–free" and discrete "bound–bound" fluorescence transitions of the NaK molecule observed upon laser excitation at $\lambda = 488$ nm: (**a**) part of the spectrum; (**b**) enlargement of three discrete vibrational bands; (**c**) level scheme [2.18]

2.7 Transition Probabilities

The intensities of spectral lines depend not only on the population density of the molecules in the absorbing or emitting level but also on the transition probabilities of the corresponding molecular transitions. If these probabilities are known, the population density can be obtained from measurements of line intensities. This is very important, for example, in astrophysics, where spectral lines represent the main source of information from the extraterrestrial world. Intensity measurements of absorption and emission lines allow the concentration of the elements in stellar atmospheres or in interstellar space to be determined. Comparing the intensities of different lines of the same element (e.g., on the transitions $E_i \rightarrow E_k$ and $E_e \rightarrow E_k$ from different upper levels E_i, E_e to the same lower level E_k) furthermore enables us to derive the temperature of the radiation source from the relative population densities N_i, N_e in the levels E_i and E_e at thermal equilibrium according to (2.18). *All these experiments, however, demand a knowledge of the corresponding transition probabilities.*

There is another aspect that makes measurements of transition probabilities very attractive with regard to a more detailed knowledge of molecular structure. Transition probabilities derived from computed wave functions of upper and lower states are much more sensitive to approximation errors in

these functions than are the energies of these states. Experimentally determined transition probabilities are therefore well suited to test the validity of calculated approximate wave functions. A comparison with computed probabilities allows theoretical models of electronic charge distributions in excited molecular states to be improved [2.19, 2.20].

2.7.1 Lifetimes, Spontaneous and Radiationless Transitions

The probability $\mathscr{P}_{ik}$ that an excited molecule in the level E_i makes a transition to a lower level E_k by spontaneous emission of a fluorescence quantum $h\nu_{ik} = E_i - E_k$ is, according to (2.17), related to the Einstein coefficient A_{ik} by

$$d\mathscr{P}_{ik}/dt = A_{ik} .$$
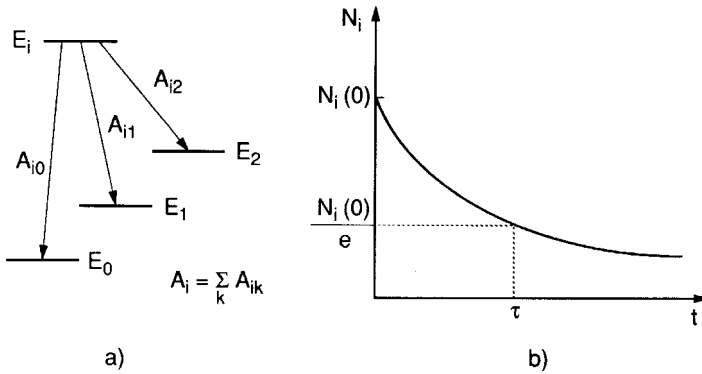
Fig. 2.17a,b. Radiative decay of the level $|i\rangle$: (**a**) Level scheme; (**b**) decay curve $N_i(t)$

When several transition paths from E_i to different lower levels E_k are possible (Fig. 2.17), the total transition probability is given by

$$A_i = \sum_k A_{ik} . \tag{2.46}$$

The decrease dN_i of the population density N_i during the time interval dt due to radiative decay is then

$$dN_i = -A_i N_i \, dt . \tag{2.47}$$

Integration of (2.47) yields

$$N_i(t) = N_{i0} e^{-A_i t} , \tag{2.48}$$

where N_{i0} is the population density at $t = 0$.

After the time $\tau_i = 1/A_i$ the population density N_i has decreased to $1/e$ of its initial value at $t = 0$. The time τ_i represents the *mean spontaneous lifetime*

of the level E_i as can be seen immediately from the definition of the mean time

$$\overline{t_i} = \int_0^\infty t \mathcal{P}_i(t) \, dt = \int_0^\infty t A_i \, e^{-A_i t} \, dt = \frac{1}{A_i} = \tau_i \, , \tag{2.49}$$

where $\mathcal{P}_i(t) \, dt$ is the probability that one atom in the level E_i makes a spontaneous transition within the time interval between t and $t + dt$.

The *radiant power* emitted from N_i molecules on the transition $E_i \rightarrow E_k$ is

$$P_{ik} = N_i h \nu_{ik} A_{ik} \, . \tag{2.50}$$

If several transitions $E_i \rightarrow E_k$ from the same upper level E_i to different lower levels E_k are possible, the radiant powers of the corresponding spectral lines are proportional to the product of the Einstein coefficient A_{ik} and the photon energy $h\nu_{ik}$. The relative radiation intensities in a certain direction may also depend on the spatial distribution of the fluorescence, which can be different for the different transitions.

The level E_i of the molecule A can be depopulated not only by spontaneous emission but also by collison-induced *radiationless* transitions (Fig. 2.18). The probability $d\mathcal{P}_{ik}^{coll}/dt$ of such a transition depends on the density N_B of the collision partner B, on the mean relative velocity $\overline{v}$ between A and B, and on the collision cross section σ_{ik}^{coll} for an inelastic collision that induces the transition $E_i \rightarrow E_k$ in the molecule A

$$d\mathcal{P}_{ik}^{coll}/dt = \overline{v} N_B \sigma_{ik}^{coll} \, . \tag{2.51}$$

When the excited molecule $A(E_i)$ is exposed to an intense radiation field, the *induced emission* may become noticeable. It contributes to the depopulation
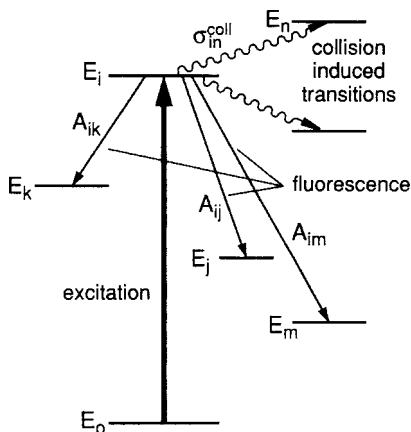
Fig. 2.18. Fluorescence- and collision-induced decay channels of an excited level $|i\rangle$

of level E_i in a transition $|i\rangle \to |k\rangle$ with the probability

$$\mathrm{d}\mathcal{P}_{ik}^{\mathrm{ind}}/\mathrm{d}t = \rho(\nu_{ik})B_{ik} . \tag{2.52}$$

The total transition probability that determines the effective lifetime of a level E_i is then the sum of spontaneous, induced, and collisional contributions, and the mean lifetime τ_i^{eff} becomes

$$\frac{1}{\tau_i^{\mathrm{eff}}} = \sum_k \left[A_{ik} + \rho(\nu_{ik})B_{ik} + N_{\mathrm{B}}\sigma_{ik}\overline{v} \right] . \tag{2.53}$$

Measuring the effective lifetime τ_i^{eff} as a function of the exciting radiation intensity and also its dependence on the density N_{B} of collision partners (Stern–Vollmer plot) allows one to determine the three transition probabilities separately (Vol. 2, Sect. 8.3).

2.7.2 Semiclassical Description: Basic Equations

In the semiclassical description, the radiation incident upon an atom is described by a classical electromagnetic (EM) plane wave

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos(\omega t - kz) . \tag{2.54a}$$

The atom, on the other hand, is treated quantum-mechanically. In order to simplify the equations, we restrict ourselves to a two-level system with the eigenstates E_a and E_b (Fig. 2.19).

Until now laser spectroscopy was performed in spectral regions where the wavelength λ was large compared to the diameter d of an atom (e.g., in the visible spectrum λ is 500 nm, but d is only about 0.5 nm). For $\lambda \gg d$, the phase of the EM wave does not change much within the volume of an atom because $kz = (2\pi/\lambda)z \ll 1$ for $z \leq d$. We can therefore neglect the spatial derivatives of the field amplitude (dipole approximation). In a coordinate system with its origin in the center of the atom, we can assume $kz \simeq 0$ within the
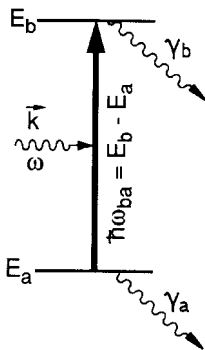
Fig. 2.19. Two-level system with open decay channels into other levels interacting with an EM field

atomic volume, and write (2.54a) in the form

$$E = E_0 \cos \omega t = A_0(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t}) \qquad \text{with} \quad |A_0| = \tfrac{1}{2}E_0 . \tag{2.54b}$$

The Hamiltonian operator

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V} , \tag{2.55}$$

of the atom interacting with the light field can be written as a sum of the un-perturbed Hamiltonian $\mathcal{H}_0$ of the free atom without the light field plus the perturbation operator $\mathcal{V}$, which describes the interaction of the atom with the field and which reduces in the *dipole approximation* to

$$\mathcal{V} = \boldsymbol{p} \cdot \boldsymbol{E} = \boldsymbol{p} \cdot \boldsymbol{E}_0 \cos \omega t , \tag{2.56}$$

where $\mathcal{V}$ is the scalar product of the dipole operator $\boldsymbol{p} = -e \cdot \boldsymbol{r}$ and the electric field $\boldsymbol{E}$.

The radiation field causes transitions in the atom. This means that the eigenfunctions of the atom become time-dependent. The general solution $\psi(\boldsymbol{r}, t)$ of the time-dependent Schrödinger equation

$$\mathcal{H}\psi = \mathrm{i}\hbar\frac{\partial\psi}{\partial t} \tag{2.57}$$

can be expressed as a linear superposition

$$\psi(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} c_n(t)u_n(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}E_n t/\hbar} , \tag{2.58}$$

of the eigenfunctions of the unperturbed atom

$$\phi_n(r, t) = u_n(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}E_n t/\hbar} . \tag{2.59}$$

The spatial parts $u_n(\boldsymbol{r})$ of these eigenfunctions are solutions of the time-independent Schrödinger equation

$$\mathcal{H}_0 u_n(\boldsymbol{r}) = E_n u_n(\boldsymbol{r}) , \tag{2.60}$$

and satisfy the orthogonality relations[1]

$$\int u_i^* u_k \,\mathrm{d}\tau = \delta_{ik} . \tag{2.61}$$

For our two-level system with the eigenstates $|a\rangle$ and $|b\rangle$ and the energies E_a and E_b, (2.58) reduces to a sum of two terms

$$\psi(\boldsymbol{r}, t) = a(t)u_a\,\mathrm{e}^{-\mathrm{i}E_a t/\hbar} + b(t)u_b\,\mathrm{e}^{-\mathrm{i}E_b t/\hbar} . \tag{2.62}$$

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[1] Note that in (2.58–2.60) a nondegenerate system has been assumed.

The coefficients $a(b)$ and $b(t)$ are the time-dependent *probability amplitudes* of the atomic states $|a\rangle$ and $|b\rangle$. This means that the value $|a(t)|^2$ gives the probability of finding the system in level $|a\rangle$ at time t. Obviously, the relation $|a(t)|^2 + |b(t)|^2 = 1$ must hold at all times t, if decay into other levels is neglected.

Substituting (2.62) and (2.55) into (2.57) gives

$$i\hbar\dot{a}(t)u_a\,e^{-iE_at/\hbar} + i\hbar\dot{b}(t)u_b\,e^{-iE_bt/\hbar} = a\mathcal{V}u_a\,e^{-iE_at/\hbar} + b\mathcal{V}u_b\,e^{-iE_bt/\hbar} ,$$
(2.63)

where the relation $\mathcal{H}_0u_n = E_nu_n$ has been used to cancel equal terms on both sides. Multiplication with $u_n^*(n = a, b)$ and spatial integration results in the following two equations

$$\dot{a}(t) = -(i/\hbar)\big[a(t)V_{aa} + b(t)V_{ab}\,e^{i\omega_{ab}t}\big] ,$$
(2.64a)
$$\dot{b}(t) = -(i/\hbar)\big[b(t)V_{bb} + a(t)V_{ba}\,e^{-i\omega_{ab}t}\big] ,$$
(2.64b)

with $\omega_{ab} = (E_a - E_b)/\hbar = -\omega_{ba}$ and with the spatial integral

$$V_{ab} = \int u_a^*\mathcal{V}u_b\,d\tau = -e\mathbf{E}\int u_a^*\mathbf{r}u_b\,d\tau .$$
(2.65a)

Since $\mathbf{r}$ has odd parity, the integrals V_{aa} and V_{bb} vanish when integrating over all coordinates from $-\infty$ to $+\infty$. The quantity

$$\mathbf{D}_{ab} = \mathbf{D}_{ba} = -e\int u_a^*\mathbf{r}u_b\,d\tau ,$$
(2.65b)

is called the atomic *dipole matrix element*. It depends on the stationary wave functions u_a and u_b of the two states $|a\rangle$ and $|b\rangle$ and is determined by the charge distribution in these states.

The expectation value $\mathbf{D}_{ab}$ of the dipole matrix element for our two-level system should be distinguished from the expectation value of the dipole moment in a specific state $|\psi\rangle$

$$\mathbf{D} = -e\int \psi^*\mathbf{r}\psi\,d\tau = 0$$
(2.66a)

which is zero because the integrand is an odd function of the coordinates. Using (2.62) and the abbreviation $\omega_{ba} = (E_b - E_a)/\hbar = -\omega_{ab}$, this can be expressed by the coefficients $a(t)$ and $b(t)$, and by the matrix element $\mathbf{D}_{ab}$ as

$$\mathbf{D} = -\mathbf{D}_{ab}(a^*b\,e^{-i\omega_{ba}t} + ab^*\,e^{+i\omega_{ba}t}) = D_0\cos(\omega_{ba}t + \varphi) ,$$
(2.66b)

with

$$D_0 = D_{ab}\,|a^*b| \quad \text{and} \quad \tan\varphi = -\frac{\text{Im}\{a^*b\}}{\text{Re}\{a^*b\}} .$$

Even without the external field, the expectation value of the atomic dipole moment oscillates with the eigenfrequency ω_{ba} and the amplitude $|a^* \cdot b|$ if the

wavefunction of the atomic system can be represented by the superposition (2.65). The time average of this oscillation's dipole moment is zero!

Using (2.54b) for the EM field and the abbreviation

$$\Omega_{ab} = D_{ab}E_0/\hbar = 2D_{ab}A_0/\hbar = \Omega_{ba} \tag{2.67}$$

which depends on the field amplitude E_0 and the dipole matrix element D_{ab}, (2.64) reduces to

$$\dot{a}(t) = -(\mathrm{i}/2)\Omega_{ab}\big(\mathrm{e}^{\mathrm{i}(\omega-\omega_{ba})t} + \mathrm{e}^{-\mathrm{i}(\omega+\omega_{ba})t}\big)b(t) , \tag{2.68a}$$

$$\dot{b}(t) = -(\mathrm{i}/2)\Omega_{ab}\big(\mathrm{e}^{-\mathrm{i}(\omega-\omega_{ba})t} + \mathrm{e}^{\mathrm{i}(\omega+\omega_{ba})t}\big)a(t) . \tag{2.68b}$$

where $\omega_{ba} = -\omega_{ba} > 0$.

These are the basic equations that must be solved to obtain the probability amplitudes $a(t)$ and $b(t)$. The frequency Ω_{ab} is called the Rabi frequency. Its physical interpretation will be discussed in Sect. 2.7.6.

2.7.3 Weak-Field Approximation

Suppose that at time $t = 0$, the atoms are in the lower state E_a, which implies that $a(0) = 1$ and $b(0) = 0$. We assume the field amplitude A_0 to be sufficiently small so that for times $t < T$ the population of E_b remains small compared with that of E_a, i.e., $|b(t < T)|^2 \ll 1$. Under this *weak-field condition* we can solve (2.68) with an iterative procedure starting with $a = 1$ and $b = 0$. Using thermal radiation sources, the field amplitude A_0 is generally small enough to make the first iteration step already sufficiently accurate.

With these assumptions the first approximation of (2.68) gives

$$\dot{a}(t) = 0 , \tag{2.69a}$$
$$\dot{b}(t) = -(\mathrm{i}/2)\Omega_{ba}\big(\mathrm{e}^{\mathrm{i}(\omega_{ba}-\omega)t} + \mathrm{e}^{\mathrm{i}(\omega_{ba}+\omega)t}\big) . \tag{2.69b}$$

With the initial conditions $a(0) = 1$ and $b(0) = 0$, integration of (2.69) from 0 to t yields

$$a(t) = a(0) = 1 , \tag{2.70a}$$
$$b(t) = \left(\frac{\Omega_{ab}}{2}\right)\left(\frac{e^{\mathrm{i}(\omega-\omega_{ba})t} - 1}{\omega - \omega_{ba}} - \frac{e^{\mathrm{i}(\omega+\omega_{ba})t} - 1}{\omega + \omega_{ba}}\right) . \tag{2.70b}$$

For $E_b > E_a$ the term $\omega_{ba} = (E_b - E_a)/\hbar$ is positive. In the transition $E_a \rightarrow E_b$, the atomic system absorbs energy from the radiation field. Noticeable absorption occurs, however, only if the field frequency ω is close to the eigenfrequency ω_{ba}. In the optical frequency range this implies that $|\omega_{ba} - \omega| \ll \omega_{ba}$. The second term in (2.70b) is then small compared to the