Chapter 17
Vibronic Medium

We study the origin of gain of radiation in a vibronic medium. We find that the gain coefficient of a vibronic medium like optically pumped titanium-sapphire has a Gaussian-like shape.

We introduce a one-dimensional model of a vibronic medium that illustrates the occurrence of vibronic transitions and we describe the results of theoretical investigations. The energy of an atomic state of a vibronic medium, i.e., the energy of a vibronic state, is composed of electronic energy of an impurity ion and of vibrational energy of the host crystal. The broad frequency distribution of lattice vibrations (phonons) of a crystal together with the possibility that many phonons can be involved in an optical transition lead to two broad vibronic sidebands of the zero-phonon line. One of the bands is observable as absorption band and the other as fluorescence band. In a laser, the absorption band is used for optical pumping and the other band for stimulated transitions.

In a classical description of vibronic transitions, we make use of the classical oscillator model of an atom to describe the electronic transition in an impurity ion and attribute a vibronic transition to an atomic oscillation experiencing frequency modulation by a vibration of the host crystal.

A vibronic laser like the titanium-sapphire laser is based on a homogeneous broadening mechanism, which determines the optical transitions.

17.1 Model of a Vibronic System

We first illustrate, by the use of a simple model, the origin of vibronic coupling. We consider a TiO_2 molecule (Fig. 17.1a); x_0 is the TiO distance. We describe the potential of the 3d electron of the Ti^{3+} ion in a TiO_2 molecule by a one-dimensional square well potential of infinite height (Fig. 17.1b). We make use of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_0}\frac{\mathrm{d}^2}{\mathrm{d}\zeta^2} + E_{\mathrm{pot}}(\zeta)\right]\chi(\zeta) = E\,\chi(\zeta), \tag{17.1}$$

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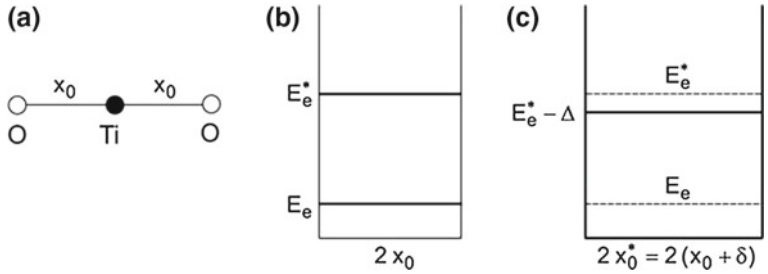

Fig. 17.1 Electronic excitation of a TiO_2 molecule. **a** TiO_2 molecule. **b** Electron in a one-dimensional potential well. **c** Excited electron in the potential well

where m_0 is the electron mass, ζ the spatial coordinate, and χ the wave function. The energy eigenvalue of the electronic ground state is equal to (Sect. 30.1)

$$E_\mathrm{e} = \frac{\pi^2\hbar^2}{8m_0x_0^2}, \tag{17.2}$$

where $2x_0$ is the width of the well. The first excited state has the energy

$$E_\mathrm{e}^* = \frac{4\pi^2\hbar^2}{8m_0x_0^2}. \tag{17.3}$$

We assume that an excitation of the 3d electron extends the TiO_2 molecule, i.e., that the TiO distance increases. The width $2x_0^*$ of the potential well corresponding to the excited state is larger than $2x_0$ and the energy of the excited state is smaller than E_e^* (Fig. 17.1c); δ is the increase of TiO distance and Δ is the decrease of energy.

The symmetric valence vibration of the TiO molecule causes a variation of the width of the potential well. The energy of the electronic ground state depends on the displacement $x - x_0$ according to the relation

$$E(x) = E_\mathrm{e} + \frac{1}{2}f(x-x_0)^2 = \frac{\pi^2\hbar^2}{8m_0x^2} + \frac{1}{2}f(x-x_0)^2 = E(x-x_0), \tag{17.4}$$

where f is a spring constant and $(1/2)f(x-x_0)^2$ is the elastic energy.

The energy of the excited state also depends on the TiO distance and therefore on the displacement $x - x_0^*$,

$$E^*(x) = E_\mathrm{e}^* + \frac{1}{2}f(x-x_0^*)^2 = \frac{4\pi^2\hbar^2}{8m_0s^2} + \frac{1}{2}f(x-x_0^*)^2 = E^*(x-x_0^*), \tag{17.5}$$

where x_0^* is the TiO distance in the excited state. We assume, for simplicity, that f has the same value as in the electronic ground state. But we take into account that the TiO distance is larger than in the case that the Ti ion is in the ground state.

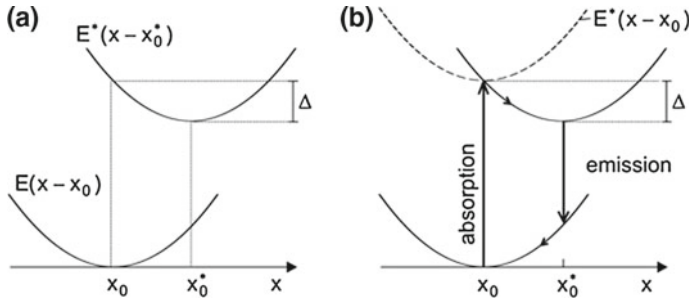

Fig. 17.2 Model of a vibronic system. **a** Vibronic energy levels. **b** Transitions between vibronic levels

Figure 17.2a (solid lines) shows parabolas describing the energy of the electronic ground state and of the excited state. The parabola describing the excited state is shifted toward larger x. According to the Franck–Condon principle, an electronic transition from the ground state to the excited state takes place without a change of the TiO distance—indicated in Fig. 17.2b as a "vertical" transition. A transition occurs to an energy that corresponds to the minimum of a parabola (dashed) that shifted in energy by the excitation energy of an electron in a rigid potential well. This energy is equal to

$$E^*(x - x_0) = \frac{4\pi^2\hbar^2}{8m_0x_0^2} + \frac{f}{2}(x - x_0)^2. \tag{17.6}$$

We assume that the change of the distance between the oxygen ions is small, $x_0^* - x_0 \ll x_0$. Then we can write (Problem 17.1)

$$E^*(x - x_0) = E_0^* - \Delta + \frac{f}{2}(x - [x_0 + \delta])^2. \tag{17.7}$$

Δ is a relaxation energy and δ is the increase of the TiO distance. After an absorption process, the TiO molecule relaxes to the equilibrium position of the excited state. Emission of a photon occurs to a vibronic state of the ground state. Another relaxation process takes the system back to the ground state.

17.2 Gain Coefficient of a Vibronic Medium

Vibronic systems have been studied in detail by the use of appropriate quantum mechanical methods [137]. The configuration diagram (Fig. 17.3a) illustrates the role of lattice vibrations. The configuration coordinate Q replaces x of our one-dimensional model. Q_0 describes, in principal, the TiO distance of the oxygen

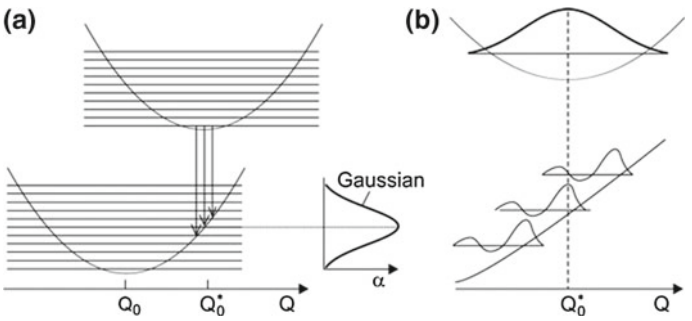

Fig. 17.3 Vibronic transitions in a crystal at low temperature. **a** Vibronic transitions and gain curve. **b** Wave functions

ions if Ti^{3+} is in its electronic ground state. Q_0^* describes the distance if Ti^{3+} is excited. $Q - Q_0$ is a measure of the displacement due to lattice vibrations; the configuration coordinate takes into account that a large number of lattice vibrations (phonons) of a crystal can couple to an electronic transition.

We discuss the gain coefficient of Ti^{3+}:Al_2O_3 at zero temperature. We make use of results obtained for vibronic transitions in Cr^{3+}:Al_2O_3 [137]. We assume that Ti^{3+}:Al_2O_3 shows a similar vibronic coupling strength as Cr^{3+}:Al_2O_3 as a comparison of the widths of the vibronic absorption bands suggests. Both Ti^{3+} and Cr^{3+} are transition metal ions; Ti^{3+} has one electron and Cr^{3+} two electrons in the 3d shell.

If the $E(Q - Q_0)$ and $E^*(Q - Q_0^*)$ curves have parabolic slopes (Fig. 17.3a), the gain coefficient $\alpha(\nu)$ is expected to have a Gaussian shape. Optical pumping leads to a population of the lowest excited-state level. Gain is due to transitions to vibronic levels of the ground state. The maximum of the gain curve corresponds, with respect to a single emission process, to emission of a photon and creation of about ten phonons of an average frequency of 7.5 THz. The halfwidth of the gain curve is about 10 times the average phonon energy. The density of states $D_1(\nu_{\text{vib}})$ of the phonons of Al_2O_3 extends from $\nu_{\text{vib}} = 0$ to a maximum vibrational frequency $h\nu_{\max}$ of about 15 THz. The Gaussian shape of the gain curve reflects the Gaussian shape of the wave function of the lowest excited state (Fig. 17.3b). According to the Franck–Condon principle, the distance does not change during an optical transition from the excited state to a vibronic state of the electronic ground state.

In an optically pumped crystal at room temperature, transitions occur also from thermally populated vibronic states (Fig. 17.4a). The population is determined by the crystal temperature. Because of additional transitions, in comparison with low temperature, the gain curve shifts to higher energy and the halfwidth is larger than at low temperature (by a factor of 1.2 according to theory [137]). Figure 17.4b shows the $E(Q - Q_0)$ and $E^*(Q - Q_0^*)$ curves together with the shape of the gain coefficient α. The gain coefficient has a Gaussian shape. Due to anharmonicity of the lattice vibrations, the $E(Q - Q_0)$ deviates from a parabolic shape at $Q > Q_0$ (dashed). This is most likely the main reason of the deviation of the gain curve from a Gaussian

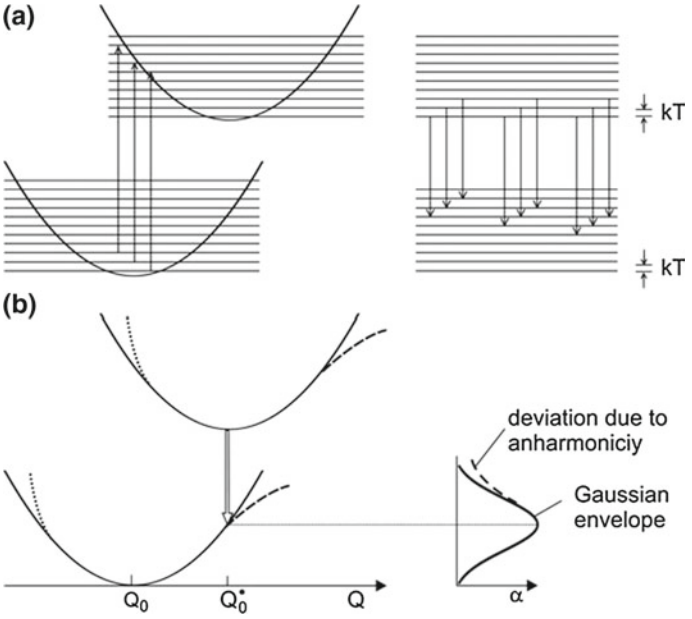

Fig. 17.4 Vibronic medium at room temperature. **a** Vibronic transitions. **b** $E(Q)$ curves and gain curves

curve at frequencies below the center frequency (*see* Fig. 7.7). Anharmonicity, occurring at room temperature, can lead to a broadening of the gain curve; the halfwidth (110 THz), derived from fluorescence data (Sect. 7.6), corresponds to about 15 times the average energy of a phonon in Al_2O_3.

While the gain curve deviates from a Gaussian shape at small frequencies, the experimental absorption curve deviates at large frequencies (*see* Fig. 7.8). This is in accordance with a deviation (Fig. 17.4, dotted) of the shape of the $E^*(Q - Q_0^*)$ curve from a parabolic shape due to anharmonicity for $Q < Q_0^*$. A structure in the absorption line, indicated in Fig. 7.8, is due to a splitting—caused by the Jahn-Teller effect [138]. The Jahn-Teller effect is most likely responsible that the absorption cross section of a Ti^{3+} ion in the ground state is by about a factor of 4 smaller than the gain cross section of an excited Ti^{3+} ion (*see* Fig. 5.3, upper part).

The maximum quantum efficiency of titanium-doped sapphire is about 80% [139].

17.3 Frequency Modulation of a Two-Level System

Instead of describing a vibronic state as a state with electronic and vibrational components, we can choose an alternative view.

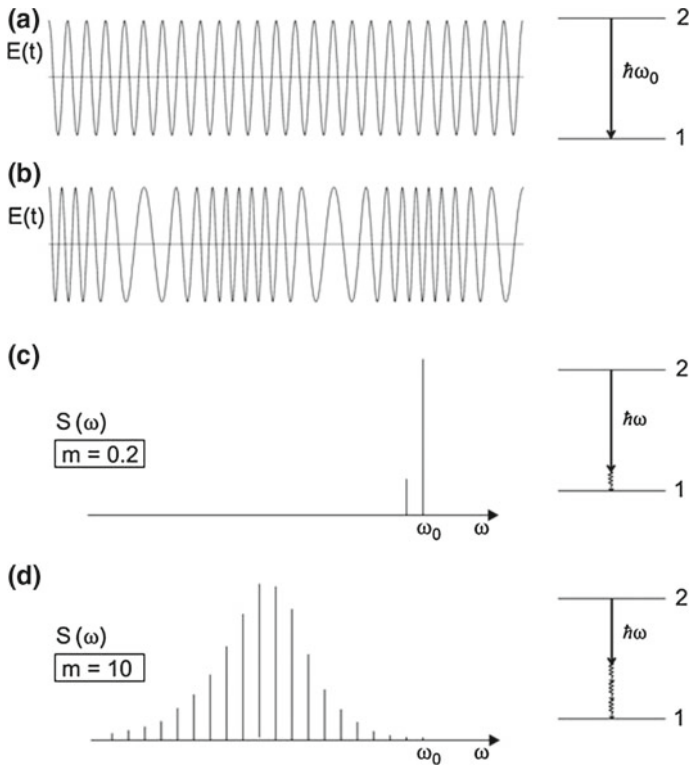

Fig. 17.5 Frequency modulation of an atomic oscillation by a lattice vibration. **a** Electric field without frequency modulation. **b** Frequency modulated electric field. **c** Luminescence spectrum at weak modulation. **d** Luminescence spectrum at strong modulation

We consider transitions between two discrete energy levels of a two-level system (with the upper level 2 and the lower level 1) of an impurity ion in a crystal at low temperature. We make use of the classical oscillator model of an atom (Sect. 4.9) and describe the electric field connected with an oscillating electron by (Fig. 17.5a)

$$E = A \cos \omega_0 t. \tag{17.8}$$

A is the amplitude of the field at the position of the electron and ω_0 the transition frequency; we assume, for simplicity, that the spontaneous lifetime is infinitely large. We now assume that a lattice vibration (frequency Ω) is present in the crystal. The vibrational wave modulates the crystalline field at the position of the impurity ion and therefore modulates the transition frequency of the electronic transition—corresponding to a *frequency modulation*. The instantaneous transition frequency is equal to

$$\omega_{\text{inst}} = \omega_0 + a \cos \Omega t, \tag{17.9}$$

where a is the maximum change of frequency toward larger and toward smaller frequency with respect to the "carrier" frequency ω_0. Due to frequency modulation, the instantaneous frequency varies periodically with time (Fig. 17.5b). It follows that the electric field is given by

$$E(t) = A \int_0^t \cos(\omega_0 + a \cos \Omega t') \mathrm{d}t' = A \cos(\omega_0 t + m \sin \Omega t), \tag{17.10}$$

where

$$m = a/\Omega \tag{17.11}$$

is the modulation degree; $m \ll 1$ corresponds to weak modulation and $m \gg 1$ to strong modulation. We make use of the relation [15]:

$$\cos(\alpha + m \sin \beta) = \sum_{n=-\infty}^{\infty} J_n(m) \cos(\alpha + n\beta). \tag{17.12}$$

J_n is the Bessel function of nth order . A Fourier transformation leads to the spectrum of the frequency modulated field [15],

$$E(\omega) = \frac{A}{2} \sum_{n=-\infty}^{\infty} J_n(m) \left(\delta(\omega - \omega_0 - n\Omega) + \delta(\omega + \omega_0 + n\Omega)\right). \tag{17.13}$$

The fluorescence spectrum is given by

$$S(\omega) = K E^2(\omega), \tag{17.14}$$

where K is a constant that depends on the electronic properties of the impurity ion and on the experimental arrangement. If the modulation is weak, the spectrum (Fig. 17.5c) consists mainly of a strong zero-phonon line at ω_0 and a weak satellite line at $\omega_0 - \Omega$. If the coupling is strong (Fig. 17.5d), we obtain a vibronic spectrum with many lines (in principle an infinitely large number). The lines around $\omega_0 - m\Omega$ are strongest; now the spectral weight of the zero-phonon line is small. We omitted in Fig. 17.5c, d the sidebands at frequencies larger than ω_0, according to the situation of a crystal at low temperature that does not contain thermally excited phonons. At low temperature, the transition frequency is modulated due to the creation of phonon waves during emission of radiation. Taking into account that we have a continuous frequency distribution of phonons, we obtain a continuous multiphonon sideband (of Gaussian shape). For information on the zero-phonon line of Ti^{3+} in Al_2O_3, *see* [138].

17.4 Vibronic Sideband as a Homogeneously Broadened Line

In an active medium of a vibronic laser like the titanium–sapphire laser, all impurity ions contribute in the same way to stimulated emission of radiation. A titanium–sapphire laser can therefore be seen as a laser that operates on a homogeneously broadened transition.

References [31, 137–139].

Problem

17.1 Determine the dependencies of Δ and δ in (17.7) on x_0 and f.