3

Interaction of Molecules with Radiation

Atoms and molecules can exist in many states that are different with respect to the electron configuration, angular momentum, parity, and energy. Transitions between these states are frequently associated with absorption or emission of electromagnetic radiation. In fact, historically, most of the insight into these different states of molecules and atoms has been gained by studying the interaction of atoms and molecules with radiation. However, interaction of radiation with matter can also be used to determine the presence and abundance of molecules or atoms in a sample.

3.1 Electromagnetic Radiation and Matter

We know electromagnetic radiation in many forms, which are solely distinguished by their wavelength or frequency (see Fig. 3.1). The wavelength λ is connected to the frequency ν by:

$$c = \nu \cdot \lambda \, ,$$

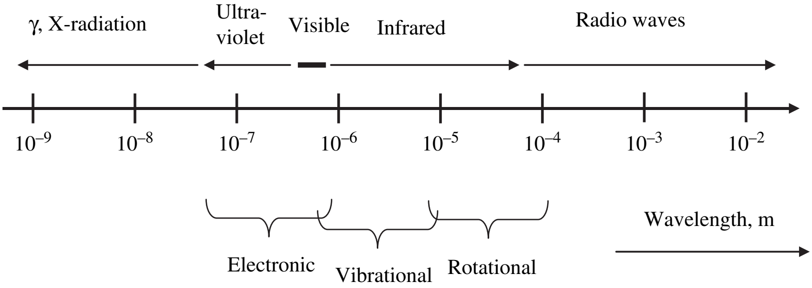

Fig. 3.1. The electromagnetic spectrum – radio waves to X-rays. The types of transition in molecules or atoms (electronic, vibrational, rotational) induced by radiation of different wavelength ranges are indicated

U. Platt and J. Stutz, *Interaction of Molecules with Radiation*. In: U. Platt and J. Stutz, Differential Optical Absorption Spectroscopy, Physics of Earth and Space Environments, pp. 77–90 (2008)
DOI 10.1007/978-3-540-75776-4_3

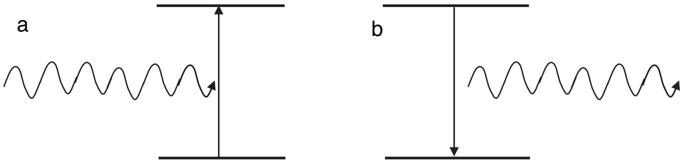

Fig. 3.2. Interaction of radiation with matter: Upon absorption of a photon with appropriate energy, the atom or molecule enters an excited state (**a**). Return to the ground state can occur by collisions with other molecules or atoms, eventually converting the photon energy into heat, or by re-radiating the photon (**b**)

where $c = 2.99792458 \times 10^8\,\mathrm{m/s} \approx 3 \times 10^8\,\mathrm{m/s}$ denotes the speed of light.

Radiation of very short wavelength ($\lambda < 30\,\mathrm{nm}$) is called γ-radiation or (at somewhat longer wavelengths) X-radiation (X-rays). At longer wavelengths, we speak of the ultraviolet and infrared ranges framing the visible spectral range extending from about 400 to 780 nm. Radiation of even longer wavelength is known as sub-mm wave ($\lambda < 1\,\mathrm{mm}$), microwave, and radio wave radiation.

It is a well-known result of quantum mechanics that some aspects of electromagnetic radiation have to be described as behaviour of waves, while others can only be understood when describing radiation as a shower of particles, the photons. Depending on the energy E of the photons, which is given by $E = h\nu = hc/\lambda$, with $h \approx 6.626176 \times 10^{-34}$ Js denoting Planck's constant, there are different forms of interaction of radiation with matter: X-rays interact largely by ionising atoms, while UV- and visible radiation will lead to reconfiguration of the outer electron shell of atoms or molecules. This process is frequently called electronic excitation. Radiation with less energy will excite vibrational or rotational states in molecular gases, as indicated in Figs. 3.1 and 3.2 and detailed in Sect. 3.3.1. Excited atoms or molecules can return to the ground state as a result of collisions with other molecules, eventually converting the energy of the absorbed photon into heat, or by re-radiating the photon (see Fig. 3.2b).

3.2 Energy Levels and Transitions in Atoms

Atoms and molecules are quantum mechanical multi-particle systems; their individual states are discrete and described by a set of quantum numbers. The states relevant to chemistry and optical spectroscopy are determined by the configuration of the outer (loosely bound) electrons.

In atoms, the energy levels E_n are determined by the quantum numbers n, l, m, s, m_s of a single outer electron, where l and m enumerate components of the orbital angular momentum of the electron, while s and m_s characterise its intrinsic angular momentum or spin. For small atoms, E is in good approximation given by the "Rydberg formula":

$$E_n = -\frac{R_\mathrm{Ry}}{n^2}, \tag{3.1}$$

where R_Ry denotes the Rydberg constant for the particular atom. Note that by convention binding energies are negative; they can be thought of the energy that was released when free electrons were attached to the nucleus (or nuclei in the case of a molecule). The energy of a photon exchanged (i.e. absorbed or emitted) by an atom (or molecule) then corresponds to the difference of the energy of two particular states. Using the famous Planck relationship between energy ΔE_el and frequency ν (and thus wavelength) of a photon we obtain:

$$\Delta E_\mathrm{el} = E_{n_1} - E_{n_2} = R_\mathrm{Ry}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu_{1,2}\ , \tag{3.2}$$

where n_1, n_2 denote the lower, upper state of the atom and $\nu_{1,2}$ the frequency of the photon, respectively. The quantity ΔE_el signifies the fact that we deal with an "electronic" transition, i.e. one where the configuration of the electron shell changes.

Frequently, the state of an atom (or molecule) is determined by several outer electrons. The relevant quantum numbers are the sum of the individual orbital angular momenta $L = \Sigma l_\mathrm{i}$, and the sum of the electron spins $S = \Sigma s_\mathrm{i}$. Also, frequently the relevant quantum number is one (j, or J) that characterises the sum of orbital angular momentum and electron spin. States with the same main quantum number n and different quantum numbers L or S (or J) have slightly different energies, the so called "fine structure" of the transitions.

3.3 Energy Levels and Transitions in Molecules

Besides electronic states of different energy, molecules have two excitation schemes not found in atoms: first, the rotation of the entire molecule and thus angular momentum of the entire molecule. The rotation of the molecule should not to be confused with the orbital angular momentum due to the electrons (which can be additionally present in molecules just as in atoms and spin of the constituent elementary particles of the molecules). Second, the vibration of the atoms within the molecule relative to each other.

The typical transition energies are:

- Electronic transitions on the order of 1 eV: corresponding wavelengths for transitions between an electronically excited state and the ground state correspond to the visible- or near UV spectral ranges.

- Vibrational transitions on the order of 0.1 eV: corresponding wavelengths for transitions between a vibrationally excited state and the ground state are in the infra red (IR) spectral range.
- Rotational transitions on the order of 10^{-3}–10^{-2} eV: corresponding wavelengths for transitions between rotationally excited state and the ground state are in the sub-mm or microwave range.

The electronic states of molecules are designated by the following (traditional) designations:

$$[\text{State}]^{2S+1}[\text{AM}]_{\Lambda+\Sigma}\ ,$$

where [State] is a code for the particular electronic state of the molecule, with [State] $= X$ denoting the lowest energy (ground) state;

- S denotes total electron spin just as in the case of atoms;
- [AM] is the code for the angular momentum. This is either the projection of the total orbital momentum on the molecule's axis or a combination of the total orbital momentum with the rotation of the molecule, depending on the coupling case. [AM] $= 1, 2, 3, \ldots$ is coded as Σ, Π, Δ, ...
- Finally, $\Lambda + \Sigma = |M_L| + M_S$ denotes the projection of the total angular momentum of the electrons on the axis connecting the nuclei of the molecule.

For instance, the ground state of the NO molecule with the angular momentum 2 and $S = 1/2$ is designated as:

$$X^2\Pi\ .$$

3.3.1 Rotational Energy Levels and Transitions

The angular momenta (total orbital angular momentum, total electron spin, "nuclear" rotation) in a molecule can couple in different ways, which are denoted as "Hund's Coupling Cases" to form a total angular momentum $\vec{J}$ and associated quantum number J.

Rotational energy levels in a molecule are given by:

$$E_j = B \cdot J(J+1)\ , \tag{3.3}$$

where $B = \frac{\hbar^2}{2\Theta}$ denotes the rotational constant of the particular molecule and rotation mode (axis) with the moment of inertia Θ with respect to this axis. In first approximation, Θ is assumed to be independent of J (rigid rotor model). However, molecules are not rigid, i.e. the atoms within a molecule can move compared to each other (see Sect. 3.3.2), therefore Θ will increase somewhat at higher values of J compared to its value at low rotational levels. As a consequence $B \propto 1/\Theta$ will decrease.

Selection rule: The difference in the angular momentum quantum number of initial and final states is given as $\Delta J = \pm 1$, since the photon exchanged with the atom/molecule has a spin (intrinsic angular momentum) of unity. The transitions are denoted as "P-branch" ($\Delta J = -1$), "Q-branch" ($\Delta J = 0$, which only can occur if electronic transitions take place at the same time), and "R-branch" ($\Delta J = +1$). Consequently, the photon energy $h\nu = \Delta E$ of allowed transitions is given by the energy difference of two consecutive states:

$$\Delta E_j = E_{j+1} - E_j = B \cdot [(J+1) \cdot (J+2) - J \cdot (J+1)] = 2B(J+1) \propto J \ . \quad (3.4)$$

In other words, the energy of absorption or emission lines varies proportionally to the rotational quantum number of the ground state; the spectra consist of lines with equidistant spacing (the energy difference of two neighbouring lines being just $2B$). The energy differences between consecutive states are on the order of $10^{-3} - 10^{-2}$ eV, the corresponding wavelengths of photons exchanged in such "purely rotational" transitions in the sub-mm- or microwave ranges. These energies are on the order of the thermal kinetic energy of molecules at room temperature, thus most molecules are rotationally excited under ambient conditions (see below).

3.3.2 Vibrational Energy Levels

Vibration of molecules can – in first approximation – be treated as harmonic oscillation, where the vibrational energy levels are given by:

$$E_\nu = \left(\nu + \frac{1}{2}\right) \cdot \hbar\omega_0 \ , \quad (3.5)$$

where $\nu = 0, 1, 2, \ldots$ denotes the vibrational quantum number (vibration level) and $1/2\hbar\omega_0$ is the zero-point energy of the molecular oscillator. Thus energies of different vibrational states vary in proportion to the vibrational quantum number ν. In addition to vibrational excitation, a molecule can also be rotationally excited (in fact is very likely to be at ambient temperatures). Thus each vibrational transition splits into a series of rotational lines (see Fig. 3.3). Energies of vibrational transitions are on the order of 0.1 eV, with the corresponding wavelengths in the IR spectral range.

3.3.3 Electronic Energy Levels

Analogous to atoms, molecules can exist in several, distinct configurations of the electronic shell; each configuration has its own set of vibrational and rotational levels, as sketched in Fig. 3.3. The situation is further complicated by the fact that the moment of inertia Θ, and thus the rotational constant B, can be different in the ground and excited electronic states (usually denoted as B'' and B', respectively). This is largely due to different inter-atomic distances in the molecule in its different electronic states. As a consequence, the rotational line spacing is no longer equidistant. Rather, the lines tend to group towards a certain wavelength either below ("blue shaded") or above ("red shaded") the wavelength given by electronic and vibrational states alone. In detail, the line positions are given by the "Fortrat Parabolas" determined by the different rotational constants (B'' and B').

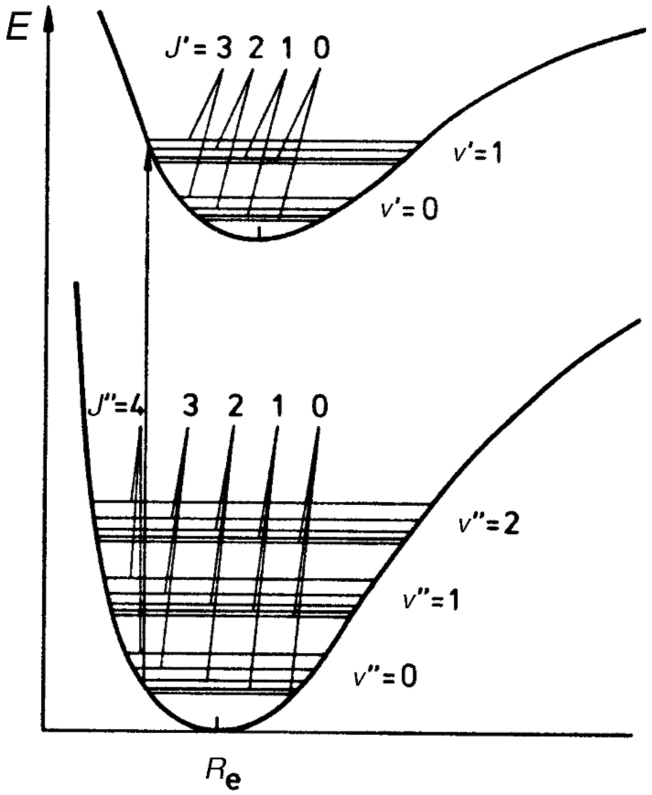

Fig. 3.3. Sketch of ro-vibrational energy levels of two electronic states of a (diatomic) molecule. Electronic energies are given as a function of the distance between the nuclei of the atoms within the molecule. They are minimal at a certain distance R_e, which is usually different in the different electronic states. The equidistant, horizontal groups of lines denote the lowest rotational levels of the vibrational states (ground state: $\nu'' = 0, 1, 2$, excited state: $\nu' = 0, 1$). Note that the energy separation of the rotational states is exaggerated in comparison to the vibrational energies

3.4 Population of States

The relative population $n(E)$ of excited states of an atom or molecule with the energies E_1, E_2 above the ground state (with $E = E_1$) is given by the **Boltzmann distribution**:

$$\frac{n\left(E_2\right)}{n\left(E_1\right)} = \frac{G_2}{G_1} \cdot \mathrm{e}^{-\frac{E_2 - E_1}{kT}} . \tag{3.6}$$

Here T denotes the absolute temperature and k the Boltzmann constant (k $=$ 1.38×10^{-23} J/K), while G_1, G_2 are the statistical weights or degeneration factors (i.e. the number of different states with the same energy E) of the respective states.

In the case of an atom, $G_n = 2n^2$, while vibrational excitation in molecules is not degenerated (i.e. $G_v = 1$). Rotational states in molecules are degenerated by $G_J = 2J + 1$, thus the population of rotational states is given by:

$$\frac{n(E_2)}{n(E_1)} = \frac{2J_2+1}{2J_1+1} \cdot \mathrm{e}^{-\frac{E_2-E_1}{kT}} = \frac{2J_2+1}{2J_1+1} \cdot \mathrm{e}^{-\frac{B(J_2(J_2+1)-J_1(J_1+1))}{kT}} . \tag{3.7}$$

With $E(J) = B \cdot J(J+1)$, where B is the rotation constant of the particular molecule and rotation axis (see above).

The kinetic energy of a molecule of around 0.03 eV at room temperature is comparable to or larger than the lowest rotational energy level, but smaller than the lowest vibrational energy level of most molecules. Therefore, several rotational states are usually populated, but only a small fraction of the molecules is vibrationally excited.

3.5 Molecular Spectra

As outlined above, the UV–visible spectra of molecules exhibit vibrational and rotational structures. Frequently, the rotational structure consists of so many lines, the spacing of which is smaller than their line-width (or which cannot be separated by the spectrometer used), thus leading to a quasi-continuous absorption within a vibrational "band". Figure 3.4 shows the cross-section spectrum of the IO molecule as an example. A striking feature of the spectrum

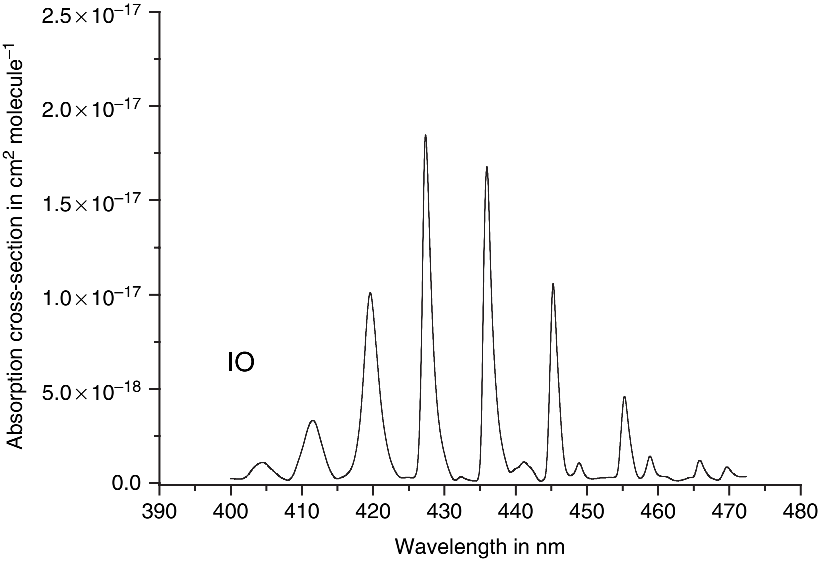

Fig. 3.4. Example of the (ro-) vibrational structure of the electronic spectrum of the iodine oxide (IO) molecule

is the quite different strength of its vibrational bands. This can be explained by the Franck–Condon principle stating that the electronic transition from the ground state to the excited state upon absorption of a photon by the molecule is much faster than the time needed for one vibration. Since the distance between the nuclei is usually different in the ground state and electronically excited state, the molecule will most likely find itself in a certain, excited vibrational state. Transitions to higher and lower vibrational states are less likely, thus having a smaller absorption cross-section, as shown in Fig. 3.4.

3.6 Broadening Mechanisms and Line Width of Absorption Lines

We first consider an excited atom or molecule with the energy E_0 above the ground state (with $E = 0$). According to classical electrodynamics, the energy of the excited electrical dipole will decrease exponentially with time t due to emission of electromagnetic radiation:

$$E(t) = E_0 \mathrm{e}^{-\delta \mathrm{t}}, \tag{3.8}$$

where δ denotes some damping constant, and $\tau = 1/\delta$ is the time in which the energy is decayed to 1/e (with e = 2.7182.. denoting the base of the natural logarithm) of its initial value. Accordingly, the corresponding amplitude of the electric field $\widehat{E}(t)$ of the emitted radiation will exponentially decrease with time t:

$$\widehat{E}(t) = \widehat{E}_0 \mathrm{e}^{-\delta \mathrm{t}} \cdot \cos\left(\omega_0 t + \varphi\right) \ . \tag{3.9}$$

Here ω_0 denotes the frequency of the oscillation, which is related to the energy E_0 of the excited state, $\omega_0 = 2\pi E_0/h$ (with h as Planck's constant), while φ is the phase of the oscillation. Since the amplitude $E(t)$ is damped, the radiation cannot be truly monochromatic. This is quantified by calculating the Fourier analysis of $E(t)$:

$$E(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} a(\omega) \mathrm{e}^{i\omega t} d\omega \ , \tag{3.10}$$

with the spectral function $a(\omega)$:

$$a(\omega) = \frac{E_0}{2} \left[\frac{\mathrm{e}^{ij}}{i\left(\omega - \omega_0\right) - \frac{\delta}{2}} - \frac{\mathrm{e}^{-ij}}{i\left(\omega + \omega_0\right) + \frac{\delta}{2}} \right] \ . \tag{3.11}$$

Since $\delta \ll \omega_0$ at frequencies ω near the resonance frequency ω_0, we can neglect the second term in the square bracket of (3.11). We obtain the radiation intensity $I(\omega)$ as the square of $a(\omega)$ (and normalising the integral over I to unity):

$$I(\omega) d\omega = I_0 \frac{\frac{\delta^2}{4}}{\left(\omega - \omega_0\right)^2 - \frac{\delta^2}{4}} d\omega \ . \tag{3.12}$$

This equation is known as the Lorentz distribution; its maximum is at $\omega = \omega_0$ while $I(\omega) = 0.5I(\omega_0)$ at $\omega = \omega_0 \pm \delta/2$, i.e. δ denotes the full width at half maximum (FWHM) of the distribution.

3.6.1 The Natural Line Width

The above described classical image of an oscillating dipole cannot directly be applied to an excited atom or molecule; however, the correspondence principle suggests that, at least at large quantum numbers, (3.12) should be a good approximation. In practice it turns out that (3.12), can be used to describe the profile of an emission line of an isolated atom when using an empirical δ. In addition, there might be more than one level which an excited atom or molecule can decay to, thus $\delta_\mathrm{L} = \Sigma\delta_\mathrm{i}$ has to be used instead of δ. The individual δ_i describe the transition frequency to the states (including the ground state) to which the excited state under consideration can decay into. Thus, we obtain the description of the **natural line shape** of an isolated atom or molecule, i.e. the intensity distribution centred at ω_0:

$$I_\mathrm{L}(\omega)d\omega = I_0 \cdot \frac{\frac{\delta_\mathrm{L}^2}{4}}{(\omega - \omega_0)^2 - \frac{\delta_\mathrm{L}^2}{4}} d\omega \;, \tag{3.13}$$

with the **natural line width** δ_L (FWHM), which essentially depends on the lifetime of the excited state of the molecule, but *not* directly on the energy difference of the transition and thus the frequency of the emitted (absorbed) radiation. For allowed transitions, the natural lifetime is on the order of 10^{-8} s, corresponding to $\delta_\mathrm{L} = 10^8$ Hz. For radiation of $\lambda = 400$ nm wavelength ($\omega = 2\pi c/\lambda \approx 4.7 \times 10^{15}$ Hz), this would amount to $\Delta\omega/\omega \approx 2.1 \times 10^{-8}$ or $\Delta\lambda \approx 8.5 \times 10^{-6}$ nm (≈ 0.01 pm).

3.6.2 Pressure Broadening (Collisional Broadening)

Collisions of molecules (among themselves or with other types of molecules in the gas) will reduce the lifetime of the excited state below the value given by the radiation transition alone, see (3.13), which determines the natural line width. The shape of a pressure broadened line is therefore Lorentzian as given in (3.12), with $\delta = \delta_\mathrm{P}$ as the width of the pressure broadened line. In principle, the collisional damping constant δ_p is given by the product of the gas kinetic collision frequency, z_AB, and the deactivation probability, p_AB, per collision (here A refers to the species under consideration, B to the gas providing the pressure). Since p_AB can be different for each molecular species, the amount of pressure broadening depends not only on the molecular species under consideration but also on the surrounding gas. Of particular interest are the self broadening (the species itself is the pressure gas, $p_\mathrm{AB} = p_\mathrm{AA}$) and air broadening (species A is occurring in traces in air, which is species B). In the latter case, the deactivation is almost exclusively occurring in collisions between air molecules and species A molecules. The collision frequency is directly proportional to the product of gas density (and thus to pressure p times T^{-1}) and to the average molecular speed (and thus to $T^{1/2}$). In summary, the pressure-broadened line width δ_{P} is therefore given by:

$$\delta_{\mathrm{P}}(p,T) = \delta_{\mathrm{P}}\left(p_0, T_0\right) \cdot \frac{p}{p_0} \cdot \sqrt{\frac{T_0}{T}} = \delta_0 \cdot \frac{p}{p_0} \cdot \sqrt{\frac{T_0}{T}} \; . \tag{3.14}$$

Here $\delta_{\mathrm{P}}(p_0, T_0) = \delta_0$ denotes the pressure broadening at some reference pressure and temperature. Typical values at one atmosphere for pressure broadening of small molecules in the near UV are $\Delta\lambda \approx 1\,\mathrm{pm}$.

3.6.3 Doppler Broadening

In reality, the atoms or molecules of a gas are not at rest but move about. This **Brownian motion** has two main consequences:

1. The energy E can be not only dissipated by radiation, but also by collisions with other molecules present in the gas. This effect manifests itself in an increased $\delta_{\mathrm{P}} > \delta_{\mathrm{L}}$, as discussed above. Since the effect can be described in terms of a damped oscillation, the line shape is also given by (3.13).
2. The Doppler effect will change the frequency ω_0 of the emitted radiation according to (in first approximation):

$$\omega = \omega_0 \cdot \left(1 + \frac{v_{\mathrm{x}}}{c}\right) \; , \tag{3.15}$$

where v_{x} denotes the velocity component of the emitting molecule with respect to the observer and c the speed of light. The distribution of an individual component of the velocity $N(v_{\mathrm{x}})dv_{\mathrm{x}}$ (denoting the number N of molecules that have the x-component of the velocity in the range of $v_{\mathrm{x}} \ldots v_{\mathrm{x}} + dv_{\mathrm{x}}$) is Gaussian (this should not be confused with the distribution of the absolute value of the velocity, which is given by the Maxwell–Boltzmann distribution).

$$N\left(v_{\mathrm{x}}\right) dv_{\mathrm{x}} = \mathrm{const} \cdot \mathrm{e}^{-\frac{m v_{\mathrm{x}}^2}{2RT}} dv_{\mathrm{x}} \; , \tag{3.16}$$

where m denotes the atomic or molecular weight (kg/mol) and R the universal gas constant. The intensity distribution centred at ω_0 follows as:

$$I_{\mathrm{D}}(\omega) d\omega = I_0 \cdot \mathrm{e}^{-\frac{mc^2}{2RT} \cdot \frac{(\omega_0 - \omega)^2}{\omega_0^2}} \cdot d\omega = I_0 \cdot \mathrm{e}^{-\frac{\delta_{\mathrm{D}}}{2} \cdot (\omega_0 - \omega)^2} \cdot d\omega \; , \tag{3.17}$$

with the FWHM of a purely Doppler broadened line:

$$\delta_{\mathrm{D}} = \omega \frac{2\sqrt{2R\ln 2}}{c} \cdot \sqrt{\frac{T}{m}} = \omega \cdot K_{\mathrm{D}} \cdot \sqrt{\frac{T}{m}} \; . \tag{3.18}$$

The constant $K_D = 2\sqrt{2R \ln 2}/c$ in the above equation has the value of $2.26 \times 10^{-8}\,(\mathrm{kg/mol})^{1/2}/\mathrm{K}^{1/2}$. For radiation with $\lambda = 400\,\mathrm{nm}$, at $T = 300\,\mathrm{K}$ and a molecular species with the molecular weight of air (0.03 kg/mol), we obtain $\delta_D/\omega_0 = \Delta\omega/\omega = 2.26 \times 10^{-8}$, or a Doppler width of $\Delta\lambda = 9 \times 10^{-4}\,\mathrm{nm}$ (about 1 pm).

3.6.4 Realistic Broadening in the UV- and Visible Spectral Ranges

Of the three broadening mechanisms discussed earlier, the natural line width, i.e. natural lifetime of the excited state, leads to very small broadening (typ. 0.01 pm), while the effect of pressure broadening and Doppler broadening are roughly equal (typ. 1 pm) in the UV–visible spectral region. Note that the two types of line shapes discussed above (Lorentzian and Gaussian) have quite different properties:

(1) The intensity (or absorption cross-section) of a Lorentzian line [e.g. (3.13)] only decays with the square of the deviation from the centre frequency $1/(\omega - \omega_0)^2$, and thus a large fraction of the total emission (or total absorption) is in the "wings" of the line. In comparison, the Gaussian profile [e.g. (3.17)] decays exponentially (proportional to $\exp[-(\omega-\omega_0)^2]$), and consequently there is very little emission (or absorption) in the wings of the line.

(2) In the case of Lorentzian (i.e. natural- or pressure) broadening, the half-width (3.13) is independent of the frequency ω (or wavelength λ), while Gaussian (i.e. Doppler) broadening (3.18) is proportional to ω (or λ). Therefore, Gaussian broadening is, under atmospheric conditions, usually negligible at low frequencies, i.e. in the far IR or microwave range, becomes noticeable in the near IR and dominates in the short-wavelength UV.

As can be seen from the examples above the natural line width is usually negligible compared to Doppler and/or pressure broadening. In particular, in the visible and UV spectral range Doppler (Gaussian) broadening is comparable to pressure (Lorentzian) broadening. The resulting line shape can be obtained by convoluting the Gaussian and Lorentzian line shapes, which is known as Voigt shape (neglecting the natural line width):

$$I_V(\omega, \delta_D, \delta_P) = \int_{-\infty}^{\infty} I_D(\omega', \delta_D) \cdot I_P(\omega - \omega', \delta_P)\, d\omega' \,. \tag{3.19}$$

Since the convolution can only be performed by numerical calculation, approximations of the Voigt shape have been developed for describing line shapes where both broadening mechanisms contribute. Figure 3.5 shows a comparison of the three line shapes.

Since absorption is the inverse process to emission, the formulas derived above also describe the line shapes of atomic- or molecular absorption lines, and thus the absorption cross-section $\sigma(\omega)$ [or $\sigma(\lambda)$] will show the same wavelength dependence as $I(\omega)$ in (3.19).

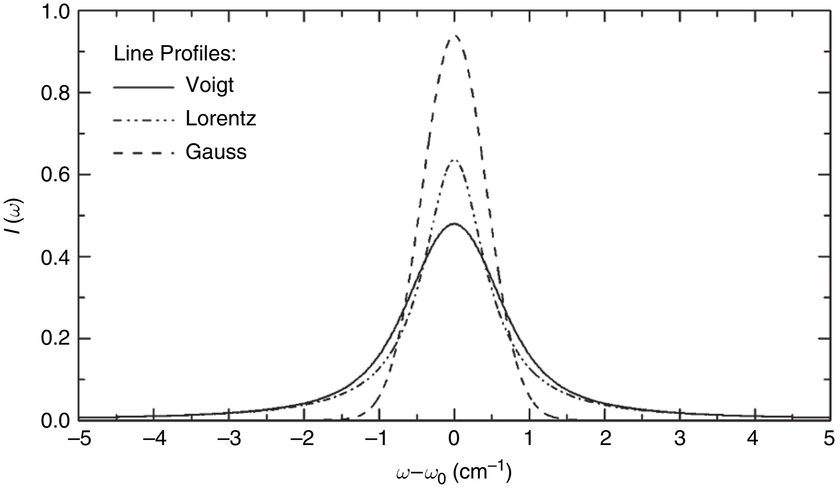

Fig. 3.5. Different line shapes: Lorentz (due to collision broadening), Doppler (due to thermal motion of molecules), and Voigt shape resulting from simultaneous Doppler and collision broadening

3.7 Spectroscopic Techniques for Chemical Analysis

The interaction of radiation with matter provides a powerful tool for a wide variety of investigations, for instance about the structure of atoms and molecules and the chemical composition of complex mixtures like the atmosphere. In principle, we distinguish between two different experimental approaches of spectroscopy:

3.7.1 The Fluorescence Techniques

The emission of radiation by excited atoms or molecules is called fluorescence. If bound states are involved in the excited state and ground state, the radiation has a characteristic set of wavelengths with the photon energy corresponding to the energy difference of the participating states (see Sects. 3.2 and 3.3).

The energy to change the molecule from the ground state to its excited state (i.e. the energy then radiated by the molecule) can be supplied by various mechanisms including thermal excitation (at ambient temperatures in the mid-infrared), electron bombardment, chemical reactions, or absorption of radiation. The latter mechanism, (light)-induced fluorescence, is employed in several measurement instruments for atmospheric trace gases (e.g. OH). A general outline of the principle is given in Fig. 3.6. In the simplest case (Fig. 3.6a), the number of fluorescence photons emitted by the molecules (or atoms) in a sample volume illuminated by the excitation radiation is proportional to the number of exciting photons multiplied by the number of trace

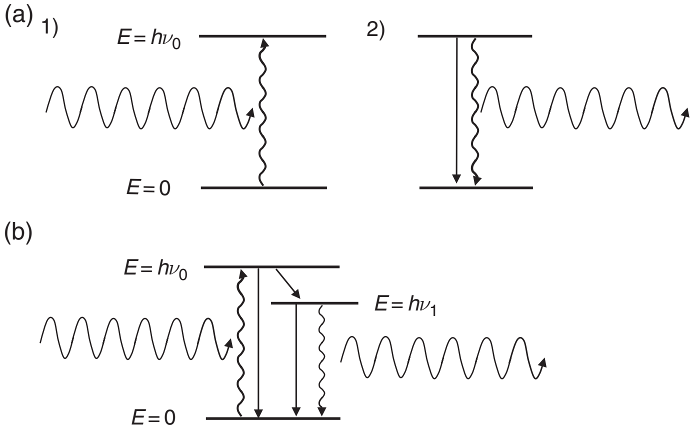

Fig. 3.6. The principle of trace gas detection by induced fluorescence spectroscopy. Scheme (**a**) uses two energy levels within the molecule, the energy difference of which is just $\Delta E = h\nu_0$. After excitation (1) by a photon with energy $E = h\nu_0$, the excited state can lose its energy (be quenched, 2) either by collision with other molecules (*straight line*) or radiating another photon with the energy $E = h\nu_0$ (*undulated line*). Scheme (**b**) uses three energy levels within the molecule. The energy difference between the lowest and the highest level is $\Delta E = h\nu_0$. After excitation by a photon with energy $E = h\nu_0$, the excited state can lose its energy completely or partially by collision with other molecules. The observed photon has a lower energy (longer wavelength) $E = h\nu_1$

gas molecules with matching transitions. In practice, geometrical factors, the absorption cross-section, and quenching also must be taken into account.

3.7.2 Absorption Spectroscopy

This spectroscopic technique makes use of the absorption of electromagnetic radiation by matter (Fig. 3.7). Quantitatively, the absorption of radiation is expressed by Lambert–Beer's law (or Bouguer–Lambert law, see Sect. 6.1):

$$I(\lambda) = I_0(\lambda) \exp[-L\sigma(\lambda)c] , \tag{3.20}$$

where $I_0(\lambda)$ denotes the initial intensity emitted by some suitable source of radiation, while $I(\lambda)$ is the radiation intensity after passing through a layer of thickness L, where the species to be measured is present at the concentration (number density) c. The quantity $\sigma(\lambda)$ denotes the absorption cross-section at the wavelength λ. The absorption cross-section is a characteristic property of any species. The absorption cross-section $\sigma(\lambda)$ can be measured in the laboratory, while the determination of the light-path length L is in many cases trivial. Once those quantities are known, the trace gas concentration c can be calculated from the measured ratio $I_0(\lambda)/I(\lambda)$:

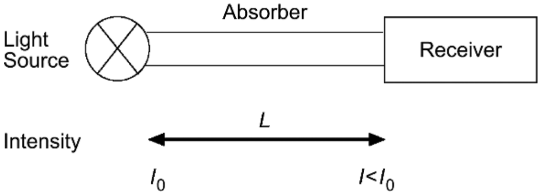

Fig. 3.7. The basic principle of absorption spectroscopic trace gas detection

$$c = \frac{\log\left(\frac{I_0(\lambda)}{I(\lambda)}\right)}{\sigma(\lambda) \cdot L} = \frac{D}{\sigma(\lambda) \cdot L} \ . \tag{3.21}$$

The expression

$$D = \log\left(\frac{I_0(\lambda)}{I(\lambda)}\right) \tag{3.22}$$

is called the **optical density** of a layer of a given species. (Note that in the literature, the decadic as well as the natural logarithm are used in the definition of the optical density. In this book we always use the natural logarithm.)