An Introduction to Raman Spectroscopy

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By

Boris A. Kolesov

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PREFACE

Vibrational spectroscopy, which includes infrared absorption (IR) and Raman scattering, is a powerful physical method for the study of chemical compounds – solid, liquid, and gaseous. In this, IR spectroscopy is to a greater extent an analytical method, and Raman spectroscopy is a research method.

The book is addressed, first of all, to students and scientists whose interests lie in the field of research of chemical, mineralogical, biological systems. This requires from a specialist both professional knowledge in each of the named areas and a deep understanding of the processes occurring in the medium during the scattering or absorption of electromagnetic radiation. For this reason, in the book, in addition to general information from the field of solid-state physics, much attention is paid to the description of those physical phenomena that have long been worked out in detail and are considered as if they do not require additional explanations. These include the concepts of a harmonic oscillator, vibration symmetry, anharmonicity, etc. These phenomena, however, underlie vibrational spectroscopy, are implicitly present in every vibrational spectrum, and their clear understanding is necessary at any level of work with vibrational spectra. The presentation is conducted at an extremely simple level that provides an understanding of the essence of the phenomenon, sometimes at the expense of a rigorous theoretical description. A small exception is only the first two chapters, where the theory of light scattering and the theory of vibrations are presented. But here, too, a general outline of the theory is given and many details are omitted. This is done in part to prevent the reader from wanting to close the book on the second page.

The text contains a large number of Raman spectra of compounds – organic and inorganic. All of them were obtained in the course of the author's work.

The author will be grateful for the comments and feedback sent to the address: kolesov@niic.nsc.ru

CHAPTER 1

RAMAN SCATTERING: BASIC CONCEPTS AND BRIEF THEORETICAL DESCRIPTION

1.1. Elastic and inelastic light scattering

Vibrational spectroscopy is actually the only physical method representing information on the pair potential of interactions between atoms. This information is embedded in the vibrational frequencies of the system. The vibrational spectrum of a compound can be obtained by infrared absorption spectroscopy or Raman scattering[1]. These experiments are characterized by different selection rules and therefore perfectly complement each other.

Let us briefly consider the processes yielding to the occurrence of both effects. Let there be a polar two-atomic molecule and an electromagnetic wave $\boldsymbol{E} = \boldsymbol{E}_0\cos(\omega_L t)$ with the variable frequency ω_L.

The electric field of the incident radiation interacts with the charged atoms of the molecule. When the radiation energy is small enough and is comparable to the energy of the fundamental mechanical vibrations of the molecule, a quantum of light is absorbed, and a quantum of vibration arises in the system (Fig. 1.1). More complex examples than diatomic molecules, such as systems of vibrating atoms, usually have a set of different fundamental vibrations, and in this case one can observe an infrared absorption spectrum consisting of several absorption bands.

When the energy of the incident radiation is high and approaches the energy of the allowed optical dipole transition between different electronic states of a molecule or crystal, we observe an absorption spectrum in the UV and visible regions.

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[1] Raman scattering was discovered almost simultaneously by C.V. Raman and K.S. Krishnan [1] in India and G.S. Landsberg and L.I. Mandelstam [2] in Russia in 1928.

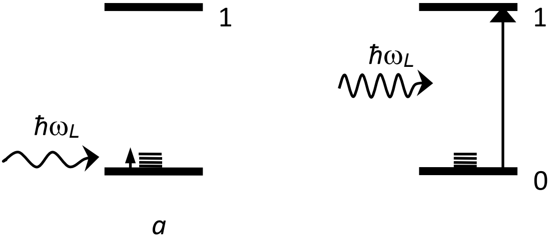

Fig. 1.1. The emergence of an absorption spectrum on vibrations (a) and electronic transitions (b)

And what happens when the energy of the electromagnetic wave is greater than the energy of atomic vibrations and less than the energy of the dipole electronic transition? In this case, the electronic subsystem is able to respond to changes in the electric field, while the atomic one is not. Under the action of an external field, the electron cloud of the molecule is displaced, forming a dipole oscillating with the frequency of the incident radiation. This process can be described as absorption of the incident wave energy by an electron and its transition to a state that is often called virtual for convenience, i.e. not a stationary state of this system[2].

It follows from the Heisenberg uncertainty relation $\Delta E \Delta t \approx \hbar$ that the lifetime of an electron in a virtual state is very small, on the order of half of the oscillation period of the electric field of the incident wave, i.e. 10^{-15} - 10^{-16} s, after which the electron is forced to leave it, emitting a quantum of light with the same energy as the energy of the incident wave, producing Rayleigh scattering (Fig. 1.2, a).

However, even in that short time that the electron is in a virtual state, due to the electron-vibrational (electron-phonon in the crystal) interaction in the system, a quantum of mechanical vibrations can arise, after which the electron returns to its initial state with the emission of a quantum of light with an energy lower than the energy of an incident photon on the energy of the emitted vibration. This process is depicted in Fig. 1.2, b. In this case, in the spectrum of scattered light, we will observe the main (i.e., upshifted Rayleigh) line ω_L and one more accompanying line with a lower frequency that differs from frequency ω_L to the frequency of the emitted quantum of the mechanical vibration.

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[2] As will be shown below, neither the classical nor the quantum mechanical description of the process of Raman scattering require the presence of a virtual state. However, its inclusion simplifies the diagram of the scattering process and makes it extremely clear.

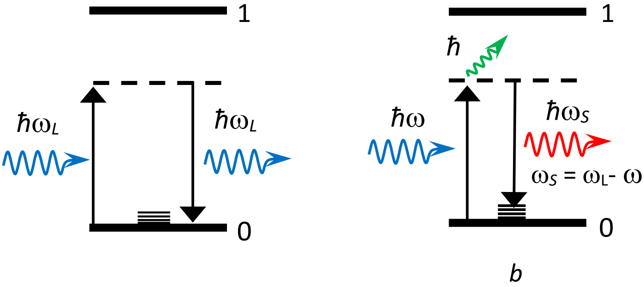

Fig. 1.2. Diagram of the appearance of elastic Rayleigh (a) and inelastic Raman (b) scattering. The emitted mechanical vibration (phonon) is marked in green $\hbar\omega$

This is spontaneous Raman scattering, or, more precisely, Stokes Raman scattering. Why Stokes? The fact is that the scattering process can be characterized not only by the generation of a vibrational quantum, but also by the elimination of a vibrational quantum already existing in the system (Fig. 1.3). In this case, the spectrum contains a line with energy higher than the energy of an incident photon on the energy of the eliminated vibration.

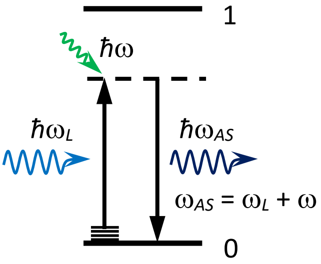

Fig. 1.3. Anti-Stokes Raman scattering

The main difference between IR absorption and Raman scattering is that the incident radiation interacts with the vibrating atoms in the first case and with their electronic subsystem in the second.

1.2. Elementary theory of Raman scattering

To elucidate the reasons for the appearance of inelastic Raman scattering on vibrations, it is necessary to consider the question of the interaction of radiation with an atomic system. The electric field of an incident electromagnetic wave

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos(\omega_L t) \tag{1.1}$$

yields to the appearance in the atomic system of an induced dipole moment

$$\boldsymbol{P} = \alpha \boldsymbol{E}. \tag{1.2}$$

If the polarizability[3] α is a time-independent constant, $\alpha = \alpha_0$, we get

$$\boldsymbol{P} = \alpha_0 \boldsymbol{E}_0 \cos(\omega_L t). \tag{1.3}$$

In other words, a dipole moment, vibrating harmonically with the same frequency ω_L arises. Such a dipole moment (Hertzian dipole) emits radiation, and the radiation energy in all directions of space per unit of time is

$$W_S = \frac{2}{3c^3}\left|\frac{d^2P}{dt^2}\right|^2 = \frac{2\omega_L^4}{3c^3}|\alpha_0|^2 E_0^2 cos^2\omega_L t \tag{1.4}$$

The dipole radiation creates coherent scattered light with constant frequency and phase. Time averaging gives

$$\overline{W}_S = \frac{2\omega_L^4}{3c^3}|\alpha_0|^2 E_0^2 \overline{cos^2\omega_L t} = \frac{\omega_L^4}{3c^3}|\alpha_0|^2 E_0^2. \tag{1.5}$$

This is the so-called Rayleigh scattering. If the scattering particles are ordered in the system, like atoms in a crystal, then the scattered light interferes in a single direction, coinciding with the direction of the incident beam in the crystal, and we observe the light passing through the crystal. Rayleigh scattering in all directions occurs precisely because of the violation of the ordered distribution of the scattering particles. For example, fluctuations in the density of a gas in the atmosphere are responsible for the sunlight scattering, and the blue color of the sky is

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[3] The term "polarizability" is used for atoms and molecules. To describe the response in solids and liquids, it is preferred to use the concept of "polarization", which is the sum of the induced dipole moments from all the particles that make up the medium. In this case, the polarization is $\boldsymbol{P} = \chi \boldsymbol{E}$, where χ is the dielectric (or simply electrical) susceptibility. The latter value is related to the molecular polarizability α by a simple relationship: $\chi = N\alpha$ (N is the number of particles per unit volume). For this reason, one can find in the literature a description of the theory of the Raman effect using the dielectric susceptibility; however, neither the essence of the effect nor the basic relations change in this case.

explained by the fourth power of the frequency in the expression for the scattering energy.

We must consider, however, what happens when the polarizability of the system (molecule, crystal) changes over time during the vibration. (The polarizability is a tensor quantity and is usually determined by the second-rank tensor. For more details, see Chapter 6.) Indeed, for a hypothetical square molecule (Fig. 1.4, a) the α_{xx} and α_{yy} components of the polarizability tensor along the *x* and *y* directions are respectively equal to each other. It is intuitively clear, however, that they become different when the molecule changes its shape during vibration (Fig. 1.4, b).

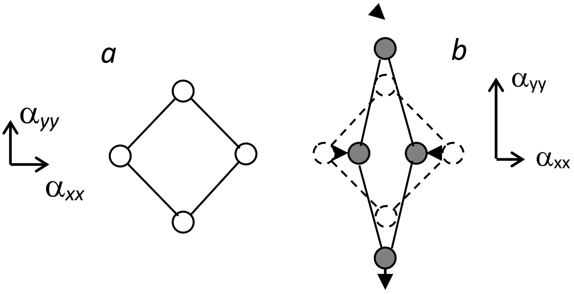

Fig. 1.4.

Polarizability of a hypothetical square molecule during rest (a) and vibration (b)

Vibrations of the system are not random, but are determined by a set of so-called normal vibrations ω_i with the corresponding normal coordinates ξ_i (definition of normal vibrations and coordinates will be given in Ch. 2). Expanding the components of the polarizability tensor in a Taylor series in normal coordinates, we obtain:

$$\alpha_{\rho\sigma} = (\alpha_{\rho\sigma})_0 + \sum_k \left(\frac{\partial \alpha_{\rho\sigma}}{\partial \xi_k}\right)_0 \xi_k + \frac{1}{2}\sum_{k,l} \left(\frac{\partial^2 \alpha_{\rho\sigma}}{\partial \xi_k \partial \xi_l}\right)_0 \xi_k \xi_l \ldots, \quad (1.6)$$

where ξ_k and ξ_l… are the normal coordinates of vibrational modes with ω_k, ω_l, etc. frequencies, and ρ, $\sigma = x, y, z$. The subscript 0 in the derivative indicates that its value is determined at the equilibrium position. In the harmonic approximation, neglecting terms with a degree ξ higher than 1, one can write

$$(\alpha_{\rho\sigma})_k = (\alpha_{\varrho\sigma})_0 + (\alpha'_{\varrho\sigma})_k \xi_k, \quad (1.7)$$

where

$$\left(\alpha'_{\varrho\sigma}\right)_k = \left(\frac{\partial \alpha_{\varrho\sigma}}{\partial \xi_k}\right)_0 \tag{1.8}$$

is the derivative of the polarizability with respect to the normal coordinate. Since relations (1.7) and (1.8) hold for all components of the polarizability tensor and the polarizability derivative, we rewrite (1.7) in a simpler form:

$$\alpha_k = \alpha_0 + \alpha'_k \xi_k. \tag{1.9}$$

Assuming a simple harmonic motion of atoms during vibrations, the dependence of ξ_k on time can be expressed as

$$\xi_k = \xi_{k0} \cos(\omega_k t + \delta_k) \tag{1.10}$$

(ξ_{k0} is the amplitude of the normal coordinate, and δ is the phase of vibration). Now we can rewrite expression (1.2) for the dipole moment in the form:

$$\boldsymbol{P} = \alpha \boldsymbol{E} = \alpha_0 \boldsymbol{E}_0 \cos(\omega_L t) + \alpha'_k \xi_{k0} \cos(\omega_k t + \delta_k) \boldsymbol{E}_0 \cos(\omega_L t). \tag{1.11}$$

Using the well-known trigonometric relation for products of cosines, we get:

$$\boldsymbol{P} = \alpha_0 \boldsymbol{E}_0 \cos(\omega_L t) + \frac{1}{2} \alpha'_k \xi_{k0}\, \boldsymbol{E}_0 \cos[(\omega_L - \omega_k)t \pm \delta_k] +$$

$$+ \frac{1}{2} \alpha'_k \xi_{k0}\, \boldsymbol{E}_0 \cos[(\omega_L + \omega_k)t \pm \delta_k]. \tag{1.12}$$

It can be seen that, in addition to the first term, which is responsible for coherent Rayleigh scattering, two additional terms appear in expression (1.12) that describe the incoherent (phase δ is random for each vibration) Raman scattering with frequencies $\omega_L - \omega_k$ (Stokes part) and $\omega_L + \omega_k$ (anti-Stokes part). As before, the Raman scattering intensity is

$$\overline{W_S} = A(\omega_L - \omega_k)^4 |\alpha'_k|^2 \boldsymbol{E}_0^2 \qquad \text{(Stokes scattering)} \tag{1.13}$$

and

$$\overline{W_S} = A(\omega_L + \omega_k)^4 |\alpha'_k|^2 \boldsymbol{E}_0^2 \quad \text{(anti-Stokes scattering)} \tag{1.14}$$

where A is constant. In both cases, the scattering intensity is proportional to the square of the amplitude of the electric field of the incident light, the square of the amplitude of the derivative of the polarizability of the system, and the fourth power of the frequency of the scattered radiation.

In conclusion, it should be noted that the simplified scheme proposed here is not a scattering theory in the full sense, and the results obtained are devoid of many important details. The only important result obtained above is the appearance of two scattering components, Stokes and anti-Stokes. However, the physics of the process of Raman scattering is much richer and it is necessary, therefore, to go to the next, higher level of the theoretical description of this phenomenon.

1.3. Semi-classic and quantum-mechanical approaches[4]

The dipole moment $\boldsymbol{P}$ induced in the system (atom, molecule, crystal) by the electric field $\boldsymbol{E}_L = \boldsymbol{e}_L^{\sigma}\boldsymbol{E}_L$ ($\boldsymbol{e}_L^{\sigma}$ – the unit vector of polarization of the incident electromagnetic wave) is

$$\boldsymbol{P} = \alpha \boldsymbol{e}_L^{\sigma} E_L. \tag{1.15}$$

Let us rewrite expression (1.4) for the energy emitted by an oscillating electric dipole $\boldsymbol{P}$ per unit time in the form:

$$\frac{dW_S}{d\Omega} = \frac{\omega_L^4}{(4\pi)^2 \varepsilon_0 c^3} \left| e_S^{\rho} \cdot \boldsymbol{P} \right|^2 = \frac{\omega_L^4}{(4\pi)^2 \varepsilon_0 c^3} \left| \boldsymbol{e}_S^{\rho} \cdot \boldsymbol{\alpha} \cdot \boldsymbol{e}_L^{\sigma} \right|^2 E_L^2, \tag{1.16}$$

where $d\Omega$ is the element spatial angle, ε_0 is the dielectric constant of the medium, $\boldsymbol{e}_S^{\rho}$ is the unit vector of polarization of the scattered radiation, and $\rho, \sigma = x, y, z$.

The scattering process is usually characterized by the differential cross section $d\sigma/d\Omega$, which can be obtained by dividing (1.16) by the energy $W_L = \varepsilon_0 c E_L^2$, falling per unit area per unit time:

$$\frac{d\sigma}{d\Omega} = \frac{\omega_L^4}{(4\pi\varepsilon_0)^2 c^4} \left| \boldsymbol{e}_S^{\rho} \cdot \boldsymbol{\alpha} \cdot \boldsymbol{e}_L^{\sigma} \right|^2 \tag{1.17}$$

In the last expression, the unknown quantity is the polarizability of the system. To find it, it is usually assumed that the scattering medium consists of a set of N electron oscillators per unit volume. Each oscillator can be represented as an electron of mass m and charge e, bonded to the

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[4] It is stated in accordance with [3].

nucleus, and this bonding is characterized by a force constant *f*. The equation of motion for such a harmonic oscillator is written in the usual way:

$$\frac{d^2x}{dt^2} + \omega_r^2 x = 0, \tag{1.18}$$

where $\omega_r^2 = f/m$ is the vibrational frequency of the oscillator (in quantum mechanics, ω_r is interpreted as the frequency at which an atom absorbs a quantum of light, i.e., the frequency of an electronic transition). For an oscillator in an external field E_L, we introduce the force $F = eE_L/m$ into expression (1.18):

$$\frac{d^2x}{dt^2} + \omega_r^2 x = F. \tag{1.19}$$

In addition, a real physical system is characterized by a finite lifetime (damping of the oscillator), which adds one more term to the equation of motion (1.19):

$$\frac{d^2x}{dt^2} + \gamma_r \frac{dx}{dt} + \omega_r^2 x = F. \tag{1.20}$$

The solution of the equation (1.20) for an electronic oscillator with a fundamental frequency ω_r and a damping coefficient γ_r, being in the electric field of an incident wave of frequency ω_L, is as follows:

$$x = \frac{(\frac{e}{m})E_L}{\omega_r^2 - \omega_L^2 - i\omega_L\gamma_r}. \tag{1.21}$$

Since $\boldsymbol{P} = \alpha\boldsymbol{E} = ex$, we get:

$$\alpha = \frac{e^2/m}{\omega_r^2 - \omega_L^2 - i\omega_L\gamma_r}. \tag{1.22}$$

Substituting (1.22) into (1.17), we obtain an expression for the scattering cross section:

$$\frac{d\sigma}{d\Omega} = \frac{r_e^2\omega_L^4}{\left(\omega_r^2 - \omega_L^2\right)^2 + \omega_L^2\gamma_r^2}\left|e_L^\sigma \cdot e_S^\rho\right|^2, \tag{1.23}$$

where $r_e = e^2/4\pi\varepsilon_0 mc^2$ is the classical radius of the electron. Far from resonance, i.e. for $\omega_L \ll \omega_r$, expression (1.23) can be rewritten as:

$$\frac{d\sigma}{d\Omega} = r_e^2 \frac{\omega_L^4}{\omega_r^4} \left| e_L^\sigma \cdot e_S^\rho \right|^2. \tag{1.24}$$

Formula (1.24) describes elastic scattering of an isotropic medium. As before, in order to obtain inelastic scattering, it is necessary to consider how the polarizability of the system changes during vibration. Each vibrational mode ω_j is characterized by the displacement of N atoms in the molecule dependent on time as $\exp(\pm i\omega_j t)$. The displacements of the k-atom in the molecule ($k = 1,2, ..., N$) $q_k^{(j)}$ can be expressed in terms of the normal coordinates ξ as will be done in Chapter 2, Eq. (2.40), but only in complex form:

$$q_k^{(j)}\left(\pm\omega_j t\right) = \boldsymbol{e}_k \xi e^{-i\omega_j t} + \boldsymbol{e}_k^* \xi^* e^{i\omega_j t}, \tag{1.25}$$

where $\boldsymbol{e}_k$ is the unit vector of displacement of the k-atom. From here, decomposing polarizability in a series in the normal coordinate ξ, we obtain a relation similar to (1.6):

$$\boldsymbol{\alpha}(\omega_L, \xi) = \boldsymbol{\alpha}(\omega_L) + \frac{\partial\boldsymbol{\alpha}}{\partial\xi}\xi e^{-i\omega_j t} + \frac{\partial\boldsymbol{\alpha}}{\partial\xi^*}\xi^* e^{i\omega_j t} + \frac{1}{2}\frac{\partial^2\boldsymbol{\alpha}}{\partial\xi^2}\xi^2 e^{-2i\omega_j t} + \frac{1}{2}\frac{\partial^2\boldsymbol{\alpha}}{\partial\xi^{*2}}\xi^{*2} e^{2i\omega_j t} + \cdots \tag{1.26}$$

Substituting (1.26) into (1.17) and restricting ourselves to the linear terms of expansion (1.26), we obtain scattering without changing the frequency ω_L (Rayleigh) and with frequency $\omega_L \pm \omega_j$ (Stokes and anti-Stokes scattering). For the last two, the differential cross-section is written as:

$$\frac{d\sigma_S}{d\Omega} = \frac{\left(\omega_L - \omega_j\right)^4}{(4\pi\varepsilon_0)^2 c^4} \left| \boldsymbol{e}_S \cdot \frac{\partial\boldsymbol{\alpha}}{\partial\xi} \cdot \boldsymbol{e}_L \right|^2 \langle\xi\xi^*\rangle \quad \text{(Stokes scattering)}, \tag{1.27}$$

$$\frac{d\sigma_{AS}}{d\Omega} = \frac{\left(\omega_L + \omega_j\right)^4}{(4\pi\varepsilon_0)^2 c^4} \left| \boldsymbol{e}_S \cdot \frac{\partial\boldsymbol{\alpha}}{\partial\xi} \cdot \boldsymbol{e}_L \right|^2 \langle\xi^*\xi\rangle \quad \text{(anti-Stokes scattering)}. \tag{1.28}$$

The factors $\langle\xi\xi^*\rangle$ and $\langle\xi^*\xi\rangle$, where the brackets denote averaging over the ground state of a molecule, are derived in quantum mechanics by replacing the displacements ξ and ξ^* with the corresponding operators ξ and $\xi^\dagger$, called the creation and annihilation operators. Omitting rather complicated quantum-mechanical calculations (see, for example, Ref. [4]), we present the final result of the calculation of the Stokes and anti-Stokes factors:

$$\langle\xi\xi^\dagger\rangle = \frac{\hbar}{2\omega_j}(n+1) \qquad \text{Stokes component}, \tag{1.29}$$

$$\langle \xi^{\dagger}\xi \rangle = \frac{\hbar}{2\omega_j} n \qquad \text{anti-Stokes component,} \qquad (1.30)$$

where *n* determines the statistical (Maxwell-Boltzmann) population of the vibrational state

$$n = \frac{1}{exp(\hbar\omega_j/kT)-1}. \qquad (1.31)$$

Substituting the last expressions in (1.27) and (1.28), we obtain:

$$\frac{d\sigma_S}{d\Omega} = \frac{\hbar(\omega_L-\omega_j)^4}{2\omega_j(4\pi\varepsilon_0)^2c^4}\left|\boldsymbol{e}_S\cdot\frac{\partial\alpha}{\partial\xi}\cdot\boldsymbol{e}_L\right|^2(n+1) \quad \text{(Stokes scattering),} \quad (1.32)$$

$$\frac{d\sigma_{AS}}{d\Omega} = \frac{\hbar(\omega_L+\omega_j)^4}{2\omega_j(4\pi\varepsilon_0)^2c^4}\left|\boldsymbol{e}_S\cdot\frac{\partial\alpha}{\partial\xi}\cdot\boldsymbol{e}_L\right|^2 n \quad \text{(anti-Stokes scattering)} \quad (1.33)$$

The fact that the anti-Stokes scattering is proportional to the number of phonons with a given energy follows from the definition of the anti-Stokes process: in order for a scattering act to occur with absorption of a phonon, this phonon must be presented in the system. But the fact that the Stokes scattering's intensity consists of two components, one of which is also proportional to the number of phonons in the system with exactly the same frequency as the scattered phonon, seems unexpected at first glance. Strange as it may seem, the well-known experiment with two identical pendulums fixed on one thread helps to understand this complex phenomenon. If an oscillation is excited in one of the pendulums, then due to the connection between them, this oscillation will be completely transferred to the second pendulum for some time, while the oscillations of the first will cease. Then the process starts in the opposite direction. Such transfer of energy from one oscillator to another and back becomes possible due to the identity of their fundamental vibrational frequencies. Now, returning to the process of light scattering by a vibration, it is easy to understand that the emitting of a phonon ω during scattering becomes much more probable if the system already has a vibration with the same frequency, which, as it were, "shakes" the system and, due to the kinematic interaction between phonons, helps the occurring of another such vibration. In the process of scattering, there is no need to transfer energy from one oscillator to another, since in this case the energy is taken from the photon. The temperature-independent part of the Stokes scattering arises due to the existence of zero-point vibrations, which provide the necessary perturbations of the system. The proportionality of the number of excitations to the number of the same excitations already presented in the system is characteristic of all particles with integer spin, i.e. bosons. From this point of view, Stokes Raman scattering is completely analogous to the well-known phenomenon of the spontaneous and stimulated emission of light. Indeed, if an atom passes into an excited electronic state, which is usually stationary, i.e. allowed, then the lifetime of this state is, nevertheless, finite, and the electron returns to the ground state with the emission of a quantum of light either under the action of zero-point oscillations of the electromagnetic field (spontaneous emission) or a quantum of an external field with the same energy (stimulated emission).

From expressions (1.32) and (1.33) we find for the ratio of the intensities of anti-Stokes I_A and Stokes I_S scattering

$$\frac{I_A}{I_S} = \frac{(\omega_L+\omega_j)^4}{(\omega_L-\omega_j)^4} exp\left(-\frac{\hbar\omega_j}{kT}\right). \tag{1.34}$$

Eq. (1.34) makes it possible to estimate the real temperature in the scattering volume of the sample (far from resonance). And since this volume is very often represented simply by a local point on the surface of a crystal or powder, the proposed method for temperature measuring is actually the only one in this case.

Returning to relations (1.27) and (1.28), it is necessary to note that their meaning is the same as that of relations (1.13) and (1.14). But, receiving both, we did not consider the dependence of the polarizability of the system (1.22) on the frequency of the incident radiation. In expression (1.22), the polarizability is represented by the scalar quantity. To preserve its tensor character, we need to multiply polarizability (1.22) by the unit tensor of the force of the electron oscillator $\boldsymbol{f_e}$ as follows:

$$\boldsymbol{\alpha} = \frac{(e^2/m)\boldsymbol{f}_e}{\omega_r^2-\omega_L^2-i\omega_L\gamma} + const. \tag{1.35}$$

Now the derivative of the polarizability with respect to the normal coordinate in (1.27) and (1.28) will consist of two contributions:

$$\frac{d\boldsymbol{\alpha}}{d\xi} = -\frac{2\omega_r\left(\frac{e^2}{m}\right)\boldsymbol{f}_e}{\left[\omega_r^2-\omega_L^2-i\omega_L\gamma\right]^2}\frac{d\omega_r}{d\xi} + \frac{\left(\frac{e^2}{m}\right)}{\omega_r^2-\omega_L^2-i\omega_L\gamma}\frac{d\boldsymbol{f}_e}{d\xi}. \tag{1.36}$$

The first term on the right-hand side of (1.36) expresses the dependence of the frequency of the electronic oscillator (energy of electronic transition) ω_r on the shift of atoms during vibration and is determined by the electron-phonon interaction. The second term represents the dependence of the oscillator strength (the intensity of the electronic transition) on the displacement of atoms. The analysis of both terms is not an easy task, and therefore we restrict ourselves here to only stating the fact that a resonance factor appears in the expression for the scattering cross section, which, after some simplifications, may look like

$$\frac{d\sigma}{d\Omega} \propto \frac{1}{\left(\omega_L^2-\omega_r^2\right)^2+\omega_L^2\gamma^2}. \qquad (1.37)$$

1.4. Quantum mechanical description

In the quantum mechanical description, the induced electric dipole of the classical theory is replaced by the dipole moment $(\boldsymbol{p})_{fi}$ of the transition from the initial state i to the final state f. But, as can be seen in Fig. 1.2, in the process of Raman scattering, both states, initial and final, are the ground electronic state of the system (i.e., $(\boldsymbol{p})_{fi} = 0$) with the only difference that the state f is vibrationally excited. At the same time, the frequency of the incident electromagnetic wave ω_L is much higher than $\omega_{if} = E_{if}/\hbar$, where E_{if} is the difference between the energies of the initial and final states. Therefore, to calculate the dipole moment of electronic transition in quantum mechanics, an intermediate state r is used, which is a real (stationary) excited electronic state of the system. In this case, the energy E_r of the excited state can be any, but it is usually assumed that ω_L is less than $\omega_r = E_r/\hbar$. The term "less" means in this case that the laser excitation frequency ω_L is spaced from the resonance frequency ω_r by many frequencies of the system ω_{if}. Under this condition, the absorption coefficient of the system (i.e., the probability of transition from the ground state to the excited electronic state) practically does not depend on the vibration of the system. At this the vibration itself can be considered as its static deformation, and the molecule can be characterized at each moment of time by the definite polarizability. The quantum mechanical scattering scheme and the designation of states are shown in Fig. 1.5.

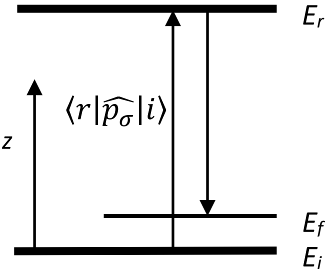

Fig. 1.5. Designation of states used in quantum mechanical calculation

Following this scheme, the dipole moment of the transition $(\boldsymbol{p}^{(1)})_{fi}$ from the initial state to the final state in the framework of approximation theory – when only the terms linear in the field $\boldsymbol{E}$ are taken into account in the intermediate expansions (as indicated by the superscript in the designation of the dipole moment) – should be proportional to both the matrix element of the transition from the initial state *i* to the intermediate state *r* and the matrix element of the transition from the state *r* to the final state *f*. G. Placek [5] showed that the ρ-component of $(\boldsymbol{p}^{(1)})_{fi}$ can be written as

$$\left(\boldsymbol{p}_\varrho^{(1)}\right)_{fi} = \frac{1}{2\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri}-\omega_L-i\Gamma_r}+\frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\varrho|i\rangle}{\omega_{ri}+\omega_L+i\Gamma_r}\right\}\tilde{E}_{\sigma 0}exp(-i\omega_S t)$$

$$+ \text{ complex conjugated,} \qquad (1.38)$$

where the summation is carried out over all formally possible intermediate states *r* (for simplicity, the entire sum can be replaced by just one state). In this expression $\hat{p}$ is the operator of the dipole moment (operator of electronic coordinate), and Γ_r is the half-width of the state r of the system, $\omega_s = \omega_L - \omega_{fi}$.

The numerator of expression (1.38) contains the matrix elements of transitions between states and, thus, describes the probabilities of system excitation and interaction with a phonon. The denominator $\omega_{ri} \pm (\omega_L + i\Gamma_r)$ is the resonance factor presented above.

Let us introduce a general expression for the ρσ-components of the polarizability $(\alpha_{\rho\sigma})_{fi}$:

$$\left(\boldsymbol{\alpha}_{\sigma\varrho}\right)_{fi} = \frac{1}{\hbar}\sum\nolimits_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_\rho|r\rangle\langle r|\hat{p}_\sigma|i\rangle}{\omega_{ri}-\omega_L-i\Gamma_r}+\frac{\langle f|\hat{p}_\sigma|r\rangle\langle r|\hat{p}_\varrho|i\rangle}{\omega_{ri}+\omega_L+i\Gamma_r}\right\}. \qquad (1.39)$$

Far from resonance $(\omega_L \ll \omega_{ri})$, the term $i\Gamma_r$ can be neglected, therefore

$$\left(\boldsymbol{\alpha}_{\sigma\varrho}\right)_{fi} = \frac{1}{\hbar}\sum_{r\neq i,f}\left\{\frac{\langle f|\hat{p}_{\rho}|r\rangle\langle r|\hat{p}_{\sigma}|i\rangle}{\omega_{ri}-\omega_{L}} + \frac{\langle f|\hat{p}_{\sigma}|r\rangle\langle r|\hat{p}_{\varrho}|i\rangle}{\omega_{ri}+\omega_{L}}\right\}. \qquad (1.40)$$

The first term in brackets is usually significantly larger than the second due to the resonant denominator, so the second term is often neglected for simplicity. Now it is necessary to substitute expression (1.40) for the polarizability into the series expansion (1.26) and, confining ourselves, as before, to the harmonic approximation, obtain the intensity of Raman scattering using relations (1.32) and (1.33). However, the transition from theoretical expressions to numerical values of intensities for molecules and crystals is still a difficult task.

The analysis presented here differs from the simplified classical scheme (§ 1.2) by the appearance of a resonance factor, which very often makes the dependence of the scattering intensity on the wavelength of the exciting radiation much stronger than the fourth power of the frequency in expressions (1.13) and (1.14). When the energy of the laser line approaches the energy of the electronic transition, the scattering intensity can increase hundreds and thousands of times (see Chapter 8). In addition, the scattering intensity turned out to depend on the thermal population of the vibrational state, which primarily affects the ratio of the intensities of the Stokes and anti-Stokes scatterings.

CHAPTER 2

VIBRATIONS OF MOLECULES

2.1. Harmonic oscillator in classical mechanics

The harmonic oscillator is an approximation that is used in physics to describe the free vibrations of various systems – mechanical, electrical, and electromagnetic. The approximation is that the restoring force acting on the system when it deviates from the equilibrium position is assumed to be linearly dependent on the magnitude of the deviation, i.e. $F = -f \cdot x$, where f is the proportionality coefficient (rigidity of spring, force constant of chemical bond). And although the last condition is satisfied only for small deviations in mechanical systems and weak fields in electromagnetic oscillations, the theory of a harmonic oscillator is fundamental in vibrational processes.

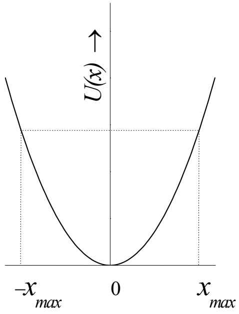

Fig. 2.1. Potential energy of a one-dimensional harmonic oscillator

We will consider a one-dimensional harmonic oscillator, in which, by definition, the potential energy $U(x)$ of one particle of mass m quadratically changes with the coordinate x (Fig. 2.1) according to the law

$$U(x) = \frac{1}{2} f x^2 , \tag{2.1}$$

and the kinetic energy takes the form

$$T(x) = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 = \frac{1}{2}m\dot{x}^2 = \frac{p^2}{2m}. \qquad (2.2)$$

Let us write the equation of motion of a harmonic oscillator:

$$m\ddot{x} = -\frac{dU}{dx} = -fx, \qquad \ddot{x} + \frac{f}{m}x = \ddot{x} + \omega^2 x = 0, \quad (2.3)$$

where $\omega = \sqrt{\frac{f}{m}}$. Solution (2.3) is either of the following two:

$$x = x_{max}\sin(\omega t + \varphi), \qquad x = x_1\cos\omega t + x_2\sin\omega t, \quad (2.4)$$

where the arbitrary constants $x_{\max}$, φ, x_1, and x_2 are related as

$$x_{max} = \sqrt{x_1^2 + x_2^2}, \qquad \operatorname{tg}\varphi = -\frac{x_2}{x_1}. \qquad (2.5)$$

(Equalities (2.5) follow from the trigonometric equation $\sin(\omega t + \varphi) = \sin\omega t \cdot \cos\varphi + \cos\omega t \cdot \sin\varphi$.) This solution describes harmonic oscillations with the frequency ω, amplitude $x_{\max}$ and initial phase φ. Angular frequency ω refers to spectroscopic frequency ν and period of vibrations T as

$$\omega = 2\pi\nu = \frac{2\pi}{T} = \sqrt{\frac{f}{m}}. \qquad (2.6)$$

For definiteness, we choose one of two solutions for the harmonic oscillator (2.4), namely

$$x = x_{max}\sin(\omega t + \varphi). \qquad (2.7)$$

$$p = m\dot{x} = m\omega x_{max}\cos(\omega t + \varphi) = p_{max}\cos(\omega t + \varphi). \qquad (2.7a)$$

From (2.1) and (2.2) we have

$$U(x) = \frac{1}{2}fx^2 = \frac{1}{2}m\omega^2 x_{max}^2\sin^2(\omega t + \varphi), \qquad (2.8)$$

$$T(x) = \frac{1}{2}m\dot{x}^2 = \frac{1}{2}m\omega^2 x_{max}^2\cos^2(\omega t + \varphi). \qquad (2.9)$$

The total energy, equal to the sum of the potential and kinetic energies, remains constant during oscillation:

$$E = T + U = \frac{1}{2} m\omega^2 x_{max}^2 \cos^2(\omega t + \varphi) + \frac{1}{2} m\omega^2 x_{max}^2 \sin^2(\omega t + \varphi) == \frac{1}{2} m\omega^2 x_{max}^2. \tag{2.10}$$

The potential energy *U* becomes equal to the total *E* at $x = \pm\, x_{max}$, therefore, the kinetic energy should vanish at these points, which are turning points for the classical oscillator. For $x = 0$, i.e. in the equilibrium position, the potential energy vanishes, and the kinetic energy reaches its maximum value. The probability of detecting an oscillating particle in a state with a coordinate *x* is maximum at the turning points $x = \pm\, x_{max}$, where the velocity of the atoms becomes equal to zero, and is minimum at the equilibrium position. The mean values of the coordinate and momentum are equal to zero because

$$\overline{x} = x_{max} \frac{1}{2\pi} \int_0^{2\pi} \sin(\omega t + \varphi) d\varphi = 0$$

$$\overline{p} = p_{max} \frac{1}{2\pi} \int_0^{2\pi} \cos(\omega t + \varphi) d\varphi = 0\,. \tag{2.11}$$

However, the mean values of the squares of the coordinate and momentum are nonzero:

$$\overline{x^2} = x_{max}^2 \frac{1}{2\pi} \int_0^{2\pi} \sin^2(\omega t + \varphi) d\varphi = \frac{x_{max}^2}{2}$$

$$\overline{p^2} = p_{max}^2 \frac{1}{2\pi} \int_0^{2\pi} \cos^2(\omega t + \varphi) d\varphi = \frac{p_{max}^2}{2}. \tag{2.12}$$

Hence, the standard deviations are:

$$\delta x = \sqrt{\overline{x^2} - (\overline{x})^2} = \frac{x_{max}}{\sqrt{2}}$$

$$\delta p = \sqrt{\overline{p^2} - (\overline{p})^2} = \frac{p_{max}}{\sqrt{2}} \tag{2.13}$$

2.2. Quantum mechanical harmonic oscillator

The solution to the problem of a quantum harmonic oscillator is directly related to the appearance of quantum mechanics. This phenomenon itself is much more complex than that of a classical oscillator. For this reason, we will first obtain a formal solution, as it is usually presented in textbooks on quantum mechanics, and then we will try to clarify the main features inherent in a quantum oscillator.

For the quantum mechanical solution of the harmonic oscillator problem, it is necessary to find the eigenvalues and eigenfunctions of the energy operator $\widehat{H}$. Introducing the generalized momentum $p = \frac{\partial T}{\partial \dot{q}} = m\dot{q}$ (q – coordinate) and taking into account expressions (2.1) and (2.2) for the kinetic and potential energies of the oscillator, we write the Hamilton function

$$\widehat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}fq^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + \frac{1}{2}fq^2. \tag{2.14}$$

Replacing the classical momentum p with the momentum operator $\hat{p} = \frac{\hbar}{i}\frac{d}{dq}$ (i.e., replacing the momentum with a mathematical operation that, acting on the function, reveals the determination of the momentum of the system), we obtain for the energy operator of the harmonic oscillator

$$\widehat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}fq^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + \frac{1}{2}fq^2. \tag{2.15}$$

The solution of an eigenvalue problem for the Schrödinger operator (stationary Schrödinger equation)

$$\widehat{H}\psi_n(q) = \left\{-\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + \frac{1}{2}fq^2\right\}\psi_n(q) = E_n\psi_n(q) \tag{2.16}$$

determines the energy spectrum

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{2.17}$$

(where $\omega = \sqrt{\frac{f}{m}}$, as in the classical oscillator, and n is the vibrational quantum number taking integer values n = 0, 1, 2, ...) and the eigenfunctions

$$\psi_n(q) = \frac{1}{N_n} H_n(\beta q) e^{-\frac{\beta^2 q^2}{2}} = \frac{1}{N_n} H_n(\xi) e^{-\frac{\xi^2}{2}}; \tag{2.18}$$

here N_n is the normalization factor, $\beta = \frac{1}{q_{max}(0)}$, $\xi = \beta q$. The functions $H(\xi)$ are Hermite polynomials of degree n ($n = 0, 1, 2 \ldots$), written as

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 + 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \\ H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12. \end{aligned} \tag{2.19}$$

Wave functions (2.18) and their squares, which determine the probability distribution of coordinate values, are shown in Fig. 2.2. It can be seen that the functions ψ_0 and ψ_2 are even with respect to the change in the sign of the coordinate, and the functions ψ_1 and ψ_3 are odd. The distribution probability is maximal at the center (i.e., in the classical equilibrium position) for the function ψ_0 and shifts towards the turning points for the remaining functions. Unlike the classical oscillator, the probability outside the classical movement is not zero, but falls off exponentially, and, in addition, it can have several maxima within the oscillator.

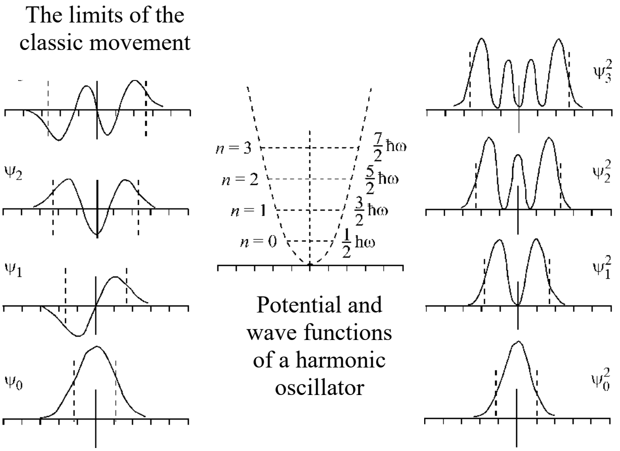

Fig. 2.2. Wave functions of a harmonic oscillator. The divisions of the abscissa scale are in units of ξ

The probability of a transition between states n and n' under the action of an electromagnetic field in the main order is determined by the dipole approximation. In this case, the disturbance potential can be considered in the form $\varphi = d \cdot E$, where d is the dipole moment equal to eq, and E is the amplitude of the electromagnetic field. Thus, in this case, the perturbation energy can be considered a linear function of q; accordingly, the transition probability will be determined by the square of the matrix element of the q coordinate between the states $|n>$ and $|n'>$

$$\langle n|q|n'\rangle = \int \psi_n q \psi_{n'} dq. \tag{2.20}$$

Using the wave functions (2.18) and (2.19), we find that, for example, the probability of the 0→1 transition will be proportional to the integral of an even function q_2 and therefore finite, and the probability of the 0→2 transition is proportional to the integral of the odd function q_3 and is equal to zero, since the integration is carried out in symmetric limits. These observations constitute a special case of the general selection rule, according to which only transitions between neighboring quantum states are allowed, i.e. with a change in the quantum number n by one

$$\Delta n = \pm 1. \tag{2.21}$$

The proof of the selection rules (2.21) is based on the fact that radiative transitions with high accuracy can be considered as dipole, in which the angular momentum of the photon is equal to $\hbar$. Consequently, the angular momentum of the oscillation during the emission or absorption of a quantum of light can change only by one, which satisfies condition (2.21).

The average values of the coordinate and momentum of stationary states of a harmonic quantum oscillator are determined by the integrals

$$\langle \psi_n|q|\psi_n\rangle = 0$$

$$\langle \psi_n|p|\psi_n\rangle = 0 \tag{2.22}$$

and are equal to zero, since the integration is carried out within symmetric limits.

In a quantum oscillator, the instantaneous values of the coordinate and momentum of a particle are not determined (these physical quantities are not observable); instead, the mean values of the squares of the coordinate and momentum are usually found. We can, however, express the amplitude of a quantum oscillator in terms of the observed parameters.