

# Chapter 4

## Radiative Processes in Molecular Gases



**Abstract** Selection rules are analyzed for vibration-rotation radiative transitions. Within the framework of the harmonic model for atomic oscillations the selection rule corresponds to a change of the vibrational number by one in radiative transitions, whereas rotational number may be conserved or be changed by one in vibrational-rotational transitions. The expression is presented for the absorption coefficient as a result of radiative vibrational-rotational transitions in diatomic molecules, as well as the expression for the spectral line intensity. The absorption coefficient is obtained for radiative vibrational-rotational transitions in atmospheres of the Earth and Venus due to atmospheric carbon dioxide molecules.

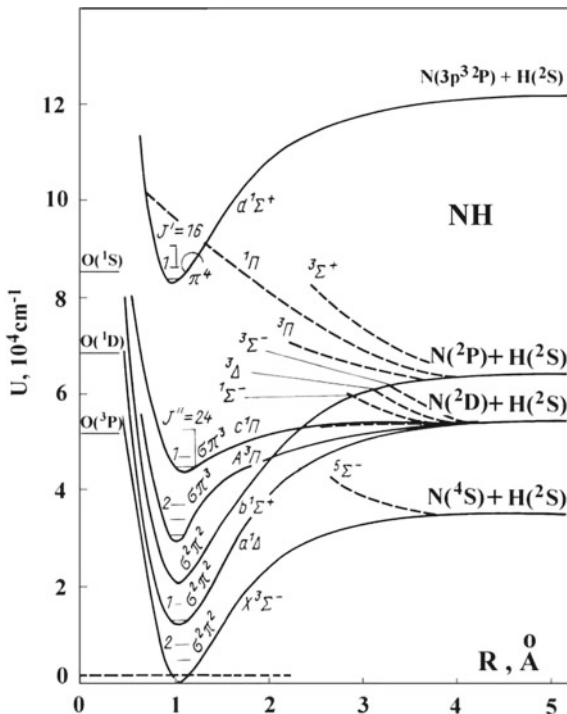
### 4.1 Selection Rules for Radiation of Molecular Gases

#### 4.1.1 *Selection Rules for One-Photon Transitions Between Vibrational States in Molecules*

Molecules consisting of bound atoms are the simplest atomic systems; their properties are determined by interaction between atoms. Large difference in masses of nuclei and electrons gives the possibility to split the problem of calculation of molecular energy levels in two parts. First we determine a surface of potential energy, i.e., energy levels at fixed positions of nuclei and obtain molecular energy with infinitely heavy nuclei which depend on the nuclear configuration. In the case of diatomic molecules the potential energy surface is the electron term (potential curve), where the molecular electron energy depends on a distance between nuclei. Analogously to infinite numbers of atomic electron levels, the infinite number of electron terms relates to each molecule. As an example of electron terms for low excited states of the NH molecule are shown in Fig. 4.1.

The other part of the molecular energy levels results from nuclear motion within a given electron term. We consider atomic nuclei as particles which interact with

**Fig. 4.1** Electron terms of the molecule NH resulted from interaction of hydrogen and nitrogen atoms. At large separation these electron terms correspond to isolated nitrogen atom which is found in various electron states, and the hydrogen atom in the ground state [1]



each other by means of some interaction potential  $U(R)$ , where  $R$  describes the sum of nuclear coordinates. Below we consider only the motion of nuclei with respect to their center of inertia which can be connected with radiative transitions. This motion within the framework of each potential well of a diatomic molecule consists of the vibrational and rotational degrees of freedom. Emission and absorption of molecules in the infrared spectrum range are determined by large number of vibrational-rotational transitions, and the molecule spectrum consists of a large number of broadened spectral lines due to these transitions. We below are restricted by diatomic and triatomic molecules where three atoms are located in the same line. Then under thermodynamic equilibrium the number density of molecules  $N_{v,J}$  in a given vibrational-rotational state is equal

$$N_{v,J} = N_o \frac{B}{T} \exp\left(-\frac{\hbar v \omega_o}{T}\right) \exp\left[-\frac{BJ(J+1)}{T}\right], \quad (4.1.1)$$

this thermodynamic equilibrium in a gas is supported by collisions involving these molecules. Here  $N_o$  is the molecular number density in the ground vibrational and rotational states,  $\hbar \omega_o$  is the excitation energy of the vibrational level,  $v$  is the quantum number of this level,  $J$  is the rotational quantum number,  $B = \hbar^2 / 2\mu \cdot r_o^2$  is the rotational constant ( $\mu$  is the reduced mass of nuclei,  $r_o$  is the distance between

nuclei),  $T$  is the gas temperature expressed in the energy units. Usually  $B \ll T$ , and below we assume this relation to be fulfilled.

Let us consider the character of interaction in diatomic molecules and its influence on radiative transitions in molecules. Evidently, the interaction potential  $U(r)$  in the molecule depends on a distance between nuclei  $r$ . Excluding the angle dependence of the wave function of nuclei, one can reduce the problem of the nuclear motion to their one-dimensional motion in the standard method by addition the centrifugal potential and introduce in this manner the effective interaction potential as

$$\hat{U}_{\text{eff}}(r) = U(r) + \frac{\hbar^2}{2\mu r^2} \hat{K}^2$$

Here  $\mu$  is the reduced mass of the molecule,  $\hat{K} = \hat{J} - \hat{L}$  is the nuclear rotational momentum, so that  $\hat{J}$  is the total molecular angular momentum,  $\hat{L}$  is the electron orbital momentum. One can average the effective interaction potential  $\hat{U}_{\text{eff}}(r)$  in the adiabatic approximation over the electron state at a fixed value of  $r$ . Thus, the effective interaction potential takes the form

$$U_{\text{eff}}(r) = U(r) + \frac{\hbar^2}{2\mu r^2} K(K+1)$$

The nuclear motion within one electron term may be described as small oscillations with respect to the equilibrium nuclear position. In the lowest order of expansion we have

$$U_{\text{eff}}(r) = U(r) + \frac{\hbar^2}{2I} K(K+1) + \frac{\mu\omega_o^2 (r - r_o)^2}{2}$$

Here  $r_o$  is the equilibrium distance between nuclei,  $I = \mu r_o^2$  is the molecular moment of inertia,  $\omega_o$  is the frequency of the classical oscillator, i.e.

$$\omega_o = \sqrt{\frac{U''(r_o)}{\mu}}$$

The last term in the expression for  $U_{\text{eff}}(r)$  presents the potential of one-dimensional harmonic oscillator. Therefore molecular energy levels are of the form

$$E_{K,v} = E_0 + \hbar\omega_0 \left( v + \frac{1}{2} \right) + \frac{\hbar^2}{2I} K(K+1); \quad v = 0, 1, 2, \dots; \quad K = 0, 1, 2, \dots \quad (4.1.2)$$

This gives the following estimation for the vibrational frequency

$$\omega_0 \sim \frac{1}{\sqrt{M}}$$

Since  $\mu \gg m_e$ , where  $m_e$  is the electron mass, typical vibrational energies are small compared to a difference between the neighboring electron terms which are of the order of an atomic unit.

Let us consider electron terms at fixed positions of nuclei and ignoring the molecular rotation. Along with the projection  $\Lambda$  of the electron orbital momentum onto the molecular axis and quantum number  $v$  of vibrational motion, it is necessary to include into consideration the projection  $\Sigma$  of the total electron spin  $S$  onto the molecular axis which values are  $\Sigma = -S, -S + 1, \dots, +S$ . The projection of the total rotational momentum of electrons on the molecular axis is  $\Omega = \Lambda + \Sigma$  and its values are  $\Omega = \Lambda + S, \Lambda + S - 1, \dots, \Lambda - S$ . Thus, an electron level with the quantum number  $\Lambda$  splits into  $2S + 1$  sublevels of the fine structure with various values of  $\Omega$ . Since the spin-orbital interaction potential is proportional to  $\hat{L}\hat{S}$ , the corresponding spin-orbital splitting can be presented as  $A(r)\Sigma$ , since the vector  $(\hat{L})$  is directed along the molecular axis. At a certain value  $\Lambda$  the electron energy is equal to  $U(r) + A(r)\Sigma$ . Hence, the energy difference of neighboring levels is the same. It should be noted that the above consideration is valid for molecules of light elements where relativistic effects are negligibly small.

We now compare the rates of radiative transitions between vibrational and electron molecular states. The difference of these rates is, on the one hand, due to difference in transition energies. On the other hand, the matrix elements of the molecular dipole moment are different. We have seen above that the ratio of photon energies for the vibrational transition  $\hbar\omega_o$  and the electron transition  $\hbar\omega_e$  is equal to

$$\frac{\hbar\omega_o}{\hbar\omega_e} \sim \sqrt{\frac{m_e}{\mu}}$$

The matrix element of the molecular dipole moment for the transition between two neighboring vibrational states is estimated as

$$\langle v | D | v - 1 \rangle = e \sqrt{\frac{\hbar v}{2\mu\omega_o}}$$

Hence, its ratio to the matrix element of the dipole moment  $D_e$  for the electron transition is of the order

$$\frac{\langle v | D | v - 1 \rangle}{D_e} = \sqrt{v \frac{m_e \omega_e}{M \omega_o}}$$

It is seen that the rates of vibrational transitions are much less than the rates of electron transitions.

One can prove that the matrix element of the dipole moment for radiation transitions between vibrational states of a diatomic molecule consisting of two identical atoms is equal to zero. We first determine the dipole moment of the molecule, considering the nuclei to be in fixed positions, and viewing these nuclei as sources of a potential field. The molecule is symmetrical for reflection with respect to the plane

which is perpendicular to the molecule axis and bisects it. In addition, the electron density also has axial symmetry with respect to the molecular axis. Therefore the electron density  $\rho$  is invariant with respect to inversion of all electrons. The dipole moment is thus

$$\mathbf{D} = \int \sum_i e \mathbf{r}_i \rho d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n = - \int \sum_i e \mathbf{r}_i \rho d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n = 0$$

for a fixed internuclear distance. Therefore, the matrix element of this operator between vibrational states is zero, and radiative vibrational transitions are absent in this case.

This conclusion holds true also, if nuclei are of different isotopes because the symmetry is determined by fields which results from interaction of these nuclei with electrons. However, this statement is violated, if the molecular rotation influences the electron state. Then the inversion symmetry of the electron wave function is lost because two nuclei have different masses. But, even for identical nuclei of a diatomic molecule this violation is not strict, because a very weak interaction of the nuclear spins with the electrons disrupts the above symmetry of the electron wave function, since two nuclear spins may have a different direction and then their influence on the electron density is different. In this case interaction of electrons with the total nuclear spin will lead to a weak mixing of electron states of opposite parity, so that dipole transitions become possible.

Let us consider the selection rules for radiative vibrational transitions in diatomic molecules which are determined by properties of the matrix element  $\langle v | \bar{\mathbf{D}} | v' \rangle$ , where  $v$  and  $v'$  are vibrational quantum numbers, and  $\bar{\mathbf{D}}$  is the dipole moment averaged over that part of the electron configuration, that does not change as a result of the dipole transition; the value  $\bar{\mathbf{D}}$  is taken at a certain distance between nuclei and then it is averaged. This corresponds to the adiabatic approximation, where the motion of the nuclei proceeds slower than the electron motion. We use that the amplitude of vibrations of nuclei is small compared to a distance between them, that allows us to employ the expansion

$$\bar{\mathbf{D}} = \bar{D}_0 + \sum_i \left( \frac{\partial \bar{\mathbf{D}}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \sum_{i,k} \left( \frac{\partial^2 \bar{\mathbf{D}}}{\partial Q_i \partial Q_k} \right)_0 Q_i Q_k + \dots \quad (4.1.3)$$

Here the  $Q_i$  are normal coordinates of nuclei, and an index  $i$  enumerates the type of vibrations. The quantity  $\bar{D}_0$  describes the dipole moment of the molecule at the equilibrium configuration of the nuclei. Derivatives of the normal coordinates are also evaluated for the equilibrium configuration.

Within the framework of the harmonic oscillator model for nuclear vibrations, we have that the matrix element of the normal coordinate  $Q_i$  for the second term of the right-hand side of relation (4.1.15) is nonzero only for transitions with a change of the vibrational quantum number  $v$  by one. This matrix element is of the form

$$\langle v | Q_i | v - 1 \rangle = \sqrt{\frac{\hbar v}{2M_i \omega_i}},$$

Here  $M_i$  is the reduced mass of the molecule for a given type of vibrations, and  $\omega_i$  is the frequency of this vibration for the mode  $i$ . As is seen from formula (4.1.15) for the mean dipole moment, transitions with a change of vibrational quantum number by two are possible owing to the third term on the right-hand side of relation (4.1.15).

We now compare the expressions for the radiative transition rates with a change of vibrational quantum number by two to those with a change by one. The ratio of the rates of these radiative transitions is given by

$$\begin{aligned} \frac{w(v \rightarrow v-2)}{w(v \rightarrow v-1)} &\sim \frac{|\langle v | \bar{\mathbf{D}} | v-2 \rangle|^2}{|\langle v | \bar{\mathbf{D}} | v-1 \rangle|^2} \sim \\ &\sim \left| \frac{\sum_{i,k} \left( \frac{\partial^2 \bar{\mathbf{D}}}{\partial Q_i \partial Q_k} \right)_0 \langle v | Q_i Q_k | v-2 \rangle}{\sum_i \left( \frac{\partial \bar{\mathbf{D}}}{\partial Q_i} \right)_0 \langle v | Q_i | v-1 \rangle} \right|^2 \sim \left| \frac{\sum_{i,k} \left( \frac{\partial^2 \bar{\mathbf{D}}}{\partial Q_i \partial Q_k} \right)_0 \sqrt{\frac{\hbar v(v-1)}{M_i M_k \omega_i \omega_k}}}{\sum_i \left( \frac{\partial \bar{\mathbf{D}}}{\partial Q_i} \right)_0 \sqrt{\frac{\hbar v}{M_i \omega_i}}} \right|^2, \end{aligned}$$

where we have used the rule of matrix multiplication

$$\langle v | Q_i Q_k | v-2 \rangle = \langle v | Q_i | v-1 \rangle \langle v-1 | Q_k | v-2 \rangle$$

The oscillator frequency is given in atomic units, it is estimated as

$$\omega_i \sim \frac{1}{\sqrt{M_i}}$$

The derivation of the dipole moment is of the order of the atomic value. Hence, we obtain the following estimation for the ratio of probabilities

$$\frac{w(v \rightarrow v-2)}{w(v \rightarrow v-1)} \sim v \sqrt{\frac{m_e}{\mu}} \quad (4.1.4)$$

Numerically, this ratio is of the order of  $10^{-2}$ – $10^{-3}$ . Thus, the most probable radiative transitions between vibrational states take place with change of the vibrational quantum number by one. Transitions with change of the vibrational quantum number by two are relatively weak if the vibrational quantum number  $v$  is not too large. The ratio of the rates (4.1.16) becomes of the order of one if the quantum number  $v$  is of the order of

$$v \sim \sqrt{\frac{\mu}{m_e}} \gg 1$$

If this criterion holds true, the vibrational energy is of the order of the electron energy,  $\hbar v \omega_i \sim \varepsilon_e$  which would imply that the harmonic oscillator approximation is not valid. Consequently, the above analysis is not suitable for this case.

Transitions with  $v \rightarrow v - 2$  also take place in the first-order term in the expansion of the dipole moment  $\bar{\mathbf{D}}$ , if we take into account the anharmonicity of the nuclear oscillations. To estimate this effect, we introduce the anharmonic term  $\alpha Q^3$  into the Hamiltonian, describing vibrations. The value of  $\alpha$  is of the order of an atomic value. For simplicity, we shall consider only one type of vibrations with the frequency  $\omega_o$ , so we below omit the indexes  $i$  and  $k$ . In the first-order perturbation theory, the correction to the harmonic wave function  $\psi_{v-2}^{(0)}$  of the state with the quantum number  $v - 2$  is of the form

$$\psi_{v-2}^{(1)} = \alpha \sum_{v'} \frac{\langle v' | Q^3 | v - 2 \rangle}{\varepsilon_{v-2}^{(0)} - \varepsilon_{v'}^{(0)}}.$$

We now extract the term with  $v' = v - 1$  (other terms with  $v' = v + 1$ ,  $v - 3$ ,  $v - 5$  have the same estimate). Then we find that the matrix element  $\langle v' | Q^3 | v - 2 \rangle$  is of the order of

$$\langle v' | Q^3 | v - 2 \rangle \sim [\langle v - 1 | Q | v - 2 \rangle]^3 \sim \left( \frac{\hbar v}{M \omega_o} \right)^{3/2}$$

and

$$\langle \psi_v^{(0)} | Q | \psi_{v-2}^{(1)} \rangle \sim \alpha \langle \psi_v^{(0)} | Q | \psi_{v-1}^{(0)} \rangle \frac{\langle v - 1 | Q^3 | v - 2 \rangle}{\varepsilon_{v-2}^{(0)} - \varepsilon_{v-1}^{(0)}} \sim \frac{\alpha}{\hbar \omega_o} \left( \frac{\hbar v}{M \omega_o} \right)^2$$

Let us estimate the ratio of the radiative transition rates

$$\frac{w(v \rightarrow v - 2)}{w(v \rightarrow v - 1)} \sim \left| \frac{\langle v | Q | v - 2 \rangle}{\langle v | Q | v - 1 \rangle} \right|^2 \sim \frac{\alpha^2}{(\hbar \omega_o)^2} \left( \frac{\hbar v}{\mu \omega_o} \right)^4 \frac{\mu \omega_o}{\hbar v} \sim \frac{v^3}{\mu^3 \omega_o^5} \sim v^3 \sqrt{\frac{m_e}{\mu}}$$

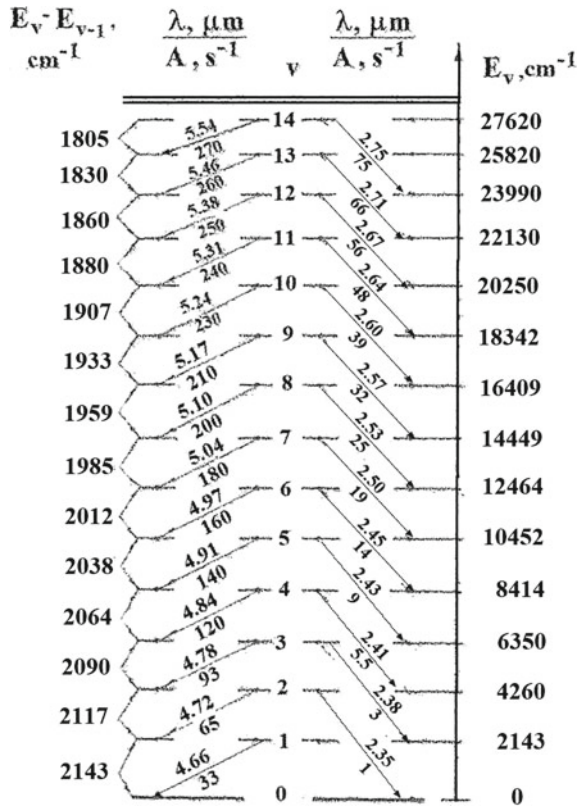
This ratio becomes of the order of one, if the vibrational quantum numbers  $v \sim (\mu/m_e)^{1/6}$ . Then the vibrational energy is of the order of

$$v \hbar \omega_o \sim \left( \frac{m_e}{\mu} \right)^{1/3} \varepsilon_e \ll \varepsilon_e$$

It is small compared to a typical electron energy  $\varepsilon_e$ . As is seen, the correction to the rate of the transition  $v \rightarrow v - 2$  due to anharmonicity of nuclear vibrations is larger than that due to the dependence of the mean dipole moment on a distance between nuclei at high vibrational quantum numbers. However, both corrections are of the same order of magnitude for small vibrational numbers  $v$ .

It is seen, that the rates for transitions with  $v \rightarrow v - 2$  and  $v \rightarrow v - 1$  become of the same order of magnitude if the correction to the wave function

**Fig. 4.2** Parameters of radiative vibrational transitions for the CO molecule [2]. Here  $E_v$  is the excitation energy of the vibration level with the vibration number  $v$ ,  $A$  is the Einstein coefficient for transition between indicated levels,  $\lambda$  is the wavelength for this transition



$$\psi_{v-2}^{(1)} \sim v^{3/2} \left(\frac{m_e}{\mu}\right)^{1/4} \psi_{v-1}^{(0)}; \quad v \sim \left(\frac{\mu}{m_e}\right)^{1/6}$$

due to anharmonicity is comparable to the unperturbed harmonic wave function  $\psi_{v-1}^{(0)}$ . The harmonic approximation is inapplicable under such circumstances, and these quantum numbers  $v$  are indeed absent even though the corresponding energies are still small compared to the typical electron energies  $\varepsilon_e$ . From the above analysis one can conclude that the vibrational number  $v$  is a “good” quantum number, the most effective radiative transitions take place with the change of  $v$  by one. But with growth of the vibrational quantum number transitions  $v \rightarrow v \pm 2$  become remarkable. This is shown in Fig. 4.2, where the rates of radiative transitions (Einstein coefficients) are given for radiative transitions of the CO molecule with the change of the vibrational quantum number both by one and by two. The results of Fig. 4.2 confirm the above conclusion that the two-photon radiative transitions between vibrational states of a diatomic molecule are weaker than the single-photon ones; however, their role rises as the vibrational quantum number increases.



### 4.1.2 Selection Rules for Transitions Between Rotational States of Diatomic Molecules

We now analyze radiative transitions between rotational states of a diatomic molecule and determine the selection rules. For the sake of simplicity, we consider first only the electron terms for which the total molecular spin is zero. We denote by  $\mathbf{J}$  the total angular momentum of the molecule in the initial state. It is composed of the orbital electron momentum and the rotational angular momentum of the nuclei. The projection of the total angular momentum on a fixed axis is denoted by  $M$ . The orbital momentum  $\Lambda$  conserves its projection onto the molecular axis at the transition due to the axial symmetry of the molecule. Since the rotational angular momentum is perpendicular to the molecular axis, then the quantity  $\Lambda$  also presents the projection of the total angular momentum of the molecule onto its axis. Analogous quantities for the final state of the molecule are marked by a prime.

Let us consider the transition  $JM \rightarrow J'M'$  between rotational states of the molecule for a given electron state, that is, for fixed quantum number  $\Lambda$ . The problem is reduced to calculation of the matrix element for the dipole moment operator. The matrix element of the component  $D_q$  (where  $q$  is a spherical component) of the dipole moment vector in the rest system can be expressed via the analogous matrix element in the rotating coordinate system in which the  $z$  axis is along the direction of the molecular axis

$$\langle J'M'\Lambda | D_q | JM\Lambda \rangle = \sqrt{\frac{2J'+1}{2J+1}} \langle J'1, M'q | JM \rangle \langle J'1, \Lambda 0 | J\Lambda \rangle \langle \Lambda | D_z | \Lambda \rangle \quad (4.1.5)$$

The index  $q$  takes the values  $0, \pm 1$ . It is clear that the matrix element of the dipole moment operator does not depend on the rotational quantum numbers in the frame of reference associated with the molecular axis; it is determined only by the electronic state of the molecule. Thus, this matrix element is diagonal with respect to rotational transition; it is equal to the mean dipole moment of the molecule,  $\bar{D} = \langle \Lambda | D_z | \Lambda \rangle$ . The selection rules for dipole rotational transitions follow from the properties of the Clebsch-Gordan coefficients contained in the (4.1.5) as

$$J - J' = \pm 1; \quad M - M' = q = 0, \pm 1 \quad (4.1.6)$$

Since the energies  $\varepsilon_J$  of the rotational states are determined by formula  $\varepsilon_J = BJ(J+1)$ , then the spontaneous transition from the state with angular momentum  $J$  to the lower state is possible only with  $J' = J - 1$ . On the basis of formula (1.2.18) for the rate of radiative processes, we obtain

$$w(J \rightarrow J' = J - 1) = \frac{4\omega_{JJ'}^3 \bar{D}^2}{3\hbar c^3} \langle J - 1, 1; \Lambda 0 | J, \Lambda \rangle^2 \sum_{M', q} \langle J - 1, 1; M', q | J, M \rangle^2 \quad (4.1.7)$$

This expression is averaged over polarizations of emitted photons and integrated over the angle of emission. When we carry out the sum in (4.1.7) and use explicit values of the Clebsch-Gordan coefficients, we find the spontaneous transition rate

$$w(J \rightarrow J-1) = \frac{32B^3 \bar{D}^2 J^2 (J^2 - \Lambda^2)}{3\hbar c^3 2J+1}; \quad B = \frac{\hbar^2}{2\mu r_o^2} \quad (4.1.8)$$

This result relates to the transition at which the vibrational and electronic states of the molecule do not change.

If the spin of the molecule is nonzero, the results must be modified somewhat. One can consider two limiting cases. If the spin interaction with the molecular axis due to spin of electrons of both atoms is large compared to the difference of neighboring rotational levels, the molecule rotation does not destroy spin coupling, and the projection of the total spin onto the molecular axis  $\Sigma$  is conserved. Then the projection of the total angular momentum onto the molecular axis is  $\Omega = \Lambda + \Sigma$ . In this case it is necessary to replace  $\Lambda$  by  $\Sigma$  in formula (4.1.8). In the opposite limiting case, where the spin interaction with the molecular axis is small compared to the difference of rotational energies for neighboring states, rotation destroys the spin-axis coupling. Then one can introduce the conserved orbital and rotational quantum numbers. The total angular momentum  $\mathbf{J} = \mathbf{K} + \mathbf{S}$  is also conserved, where  $\mathbf{S}$  is the spin vector of the molecule, and  $\mathbf{K}$  is the rotational momentum. Each rotational level splits into a multiplet with  $2S + 1$  components, which have angular momenta ranging from  $J = K - S$  to  $J = K + S$ . If we do not specify the component of the multiplet, then the total rotational transition rate is obtained from (4.1.8) by replacing  $J$  with  $K$ . However, for relative probabilities involving individual lines of the multiplet, then we obtain expressions by analogy with those in the case of radiative transitions between components of fine structure. Namely, in this case the angular momenta  $\mathbf{K}$  and  $\mathbf{S}$  are coupled by analogy to the summation of momenta  $\mathbf{L}$  and  $\mathbf{S}$  in the fine structure of light atoms. In this case there is no coupling of the angular momenta  $\mathbf{K}$  and  $\mathbf{S}$  with the molecular axis.

Let us compare the rates of radiative transitions between rotational and electronic molecular states. It follows from formula (4.1.8) for  $J \gg 1$  that

$$\frac{w_{\text{rot}}}{w_e} \sim J^3 \left( \frac{m_e}{M} \right)^3 \ll 1 \quad (4.1.9)$$

From this one can conclude that the rate of rotational transitions is small compared to that of electron ones. One can compare this with the above ratio of the rates of vibrational and electronic transitions that is given by

$$\frac{w_{\text{vib}}}{w_e} \sim \nu \left( \frac{m_e}{\mu} \right)^2 \ll 1 \quad (4.1.10)$$

Here  $v$  is the vibrational quantum number. It follows from comparison of formulas (4.1.9) and (4.1.10) that the rate of rotational transitions is less also than that of the vibrational transitions.

Let us discuss the selection rules for rotational quantum numbers in vibrational-rotational transitions with a change of the vibrational quantum number. This problem is a generalization of the previous one, where the rotational transition rate takes place without a change of the vibrational state. In that case, the matrix element of the projection of the dipole moment onto the molecular axis was equal to the mean dipole moment of the molecule at the distance  $r = r_0$  between the nuclei, where  $r_0$  is the equilibrium distance. This matrix element is zero for transitions associated with a change in vibrational state as a consequence of the orthogonality of vibrational wave functions. Therefore now we present the next term of expansion of the dipole moment averaged over an electron state over a small differences  $Q = r - r_0$ . The term proportional to  $Q$  leads to matrix elements arising from the linear harmonic oscillator coordinate that is nonzero for transitions between neighboring vibrational states only. Thus, the selection rule  $v' - v = \pm 1$  is valid for the vibrational quantum number  $v$ .

Considering the radiative vibrational-rotational transitions, we now concentrate on the change of the rotational state. For a diatomic molecule, the dipole moment operator of the molecule is directed along its axis with the unit vector  $\mathbf{n}$  in this direction. The matrix element of the dipole moment is proportional to the quantity  $\langle JM | n_q | J' M' \rangle$ , where the component  $n_q$  is connected with the vector  $\mathbf{n}$  in the same manner, as  $D_q$  relates to  $\mathbf{D}$ . Correspondingly, the rate of this spontaneous transition with a given change of quantum numbers is proportional to the square of this matrix element, i.e.,

$$w(v, J, M \rightarrow v', J', M') \sim |\langle JM | n_q | J' M' \rangle|^2,$$

where  $v, J, M$  are the vibrational quantum number, the total angular momentum of the linear molecule, and its projection onto a fixed axis in a space respectively. The primed quantities  $v', J', M'$  are the same quantum numbers for the final molecular state.

The total transition rate into all rotational states is an inverse lifetime of this state, or

$$\frac{1}{\tau} = \sum_{J', M', q} w(v, J, M \rightarrow v', J', M')$$

On the basis of the normalization condition

$$\sum_{J', M', q} |\langle JM | n_q | J' M' \rangle|^2 = \sum_q \langle JM | n_q^2 | JM \rangle = 1,$$

one can obtain from the last two expressions

$$w(v, J, M \rightarrow v', J', M') = \frac{1}{\tau} |\langle JM | n_q | J' M' \rangle|^2; \quad q = M' - M$$

**Table 4.1** The probability  $\Phi_{JM}(J', M')$  for molecular vibrational-rotational transitions

	$J' = J - 1$	$J' = J + 1$
$M' = M - 1$	$\frac{(J+M)(J+M-1)}{2(2J-1)(2J+1)}$	$\frac{(J-M+1)(J-M+2)}{2(2J+1)(2J+3)}$
$M' = M$	$\frac{J^2 - M^2}{(2J-1)(2J+1)}$	$\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)}$
$M' = M + 1$	$\frac{(J-M)(J-M-1)}{2(2J-1)(2J+1)}$	$\frac{(J+M+1)(J+M+2)}{2(2J+1)(2J+3)}$

We now calculate the matrix element from the projection of the unit vector  $n_q$ . Using the Clebsch-Gordan coefficients, one can obtain

$$\Phi_{JM}(J'M') = |\langle JM | n_q | J'M' \rangle|^2 = \frac{2J'+1}{2J+1} \langle J'1, M'q | JM \rangle^2 \langle J'1, 00 | J0 \rangle^2, \quad (4.1.11)$$

where  $q$  is equal to 0,  $-1$ ,  $+1$ . The second factor in expression (4.1.11) is nonzero only if  $J' = J \pm 1$ . Therefore the only transition is possible with a change of the rotational quantum number by one. Values of the function  $\Phi_{JM}(J'M')$  for various values of  $J'$  and  $M'$  are given in Table 4.1.

The function  $\Phi_{JM}(J'M')$  is satisfied the following sum rules

$$\sum_{M'} \Phi_{JM}(J-1, M') = \frac{J}{2J+1}; \quad \sum_{M'} \Phi_{JM}(J+1, M') = \frac{J+1}{2J+1}$$

From this we also have

$$\sum_{J'M'} \Phi_{JM}(J', M') = 1$$

One can obtain from formula (4.1.11) the average rates of the radiative spontaneous transitions  $v \rightarrow v-1$  over projections  $M'$  of the molecular angular momentum. These rates for spontaneous emission for transitions with an increase and decrease by one of the rotational quantum number  $J$  are equal

$$w(v, J \rightarrow v-1, J+1) = \frac{J+1}{2J+1} \frac{1}{\tau}, \quad w(v, J \rightarrow v-1, J-1) = \frac{J}{2J+1} \frac{1}{\tau}, \quad (4.1.12)$$

where  $\tau$  is the lifetime of the initial state due to the spontaneous radiative decay. These expressions describe spontaneous emission of photons of any polarization. Since the rate for emission of a photon with a given polarization does not depend on the direction of its polarization because of an average over projections of the total angular momentum, the rate of this process for a certain polarization is one half of the total rate.

We also consider selection rules for rotational states of triatomic linear molecules. If the oscillation takes place only in the molecular axis direction, the selection rules

**Table 4.2** Values of Clebsch-Gordan coefficient  $C_{J,m-\mu;1\mu}^{J'm'}$  for addition of momenta and their projections  $J, m'$  and  $1, \mu$  into the momentum  $J'm'$ 

Branch	$J'$	$\mu = -1$	$\mu = 0$	$\mu = +1$
P	$J - 1$	$\sqrt{\frac{(J-m')(J-m'+1)}{2(J+1)(2J+1)}}$	$\sqrt{\frac{(J-m'+1)(J+m'+1)}{(J+1)(2J+1)}}$	$\sqrt{\frac{(j+m')(j+m'+1)}{2(j+1)(2j+1)}}$
Q	$J$	$\sqrt{\frac{(J-m')(J+m'+1)}{2J(J+1)}}$	$\frac{m'}{\sqrt{J(J+1)}}$	$-\sqrt{\frac{(J+m')(J-m'+1)}{2J(2J+1)}}$
R	$J + 1$	$\sqrt{\frac{(J+m')(J+m'+1)}{2J(2J+1)}}$	$-\sqrt{\frac{(J-m')(J+m')}{J(2J+1)}}$	$\sqrt{\frac{(J-m')(J-m'+1)}{2J(2J+1)}}$

for a triatomic molecule are identical to those of a diatomic molecule. We denote below a vibrational quantum number by  $v$  and a rotational momentum by  $j$ . Our goal is to determine the rate of radiative transition  $w(v, j \rightarrow v', j')$ . Modeling vibrations in the  $\text{CO}_2$  molecule by a harmonic oscillator, we obtain the selection rule for vibrational radiative transitions  $v \rightarrow v \pm 1$  for linear molecules including the  $\text{CO}_2$  molecule. Because of a large time of radiative transitions in molecules compared with collision ones in atmospheric air, the number density of molecules  $N_j$  in a given rotational state  $J$  is determined by the Boltzmann formula

$$N_j = N_o(2J + 1) \frac{B}{T} \exp\left[-\frac{BJ(J + 1)}{T}\right], \quad (4.1.13)$$

where  $N_o$  is the total number density of molecules for this vibrational state,  $T$  is the gas temperature expressed in energetic units,  $B$  is the rotational constant,  $BJ(J + 1)$  is the excitation energy for this rotational state, and the normalized constant is taken from the condition  $B \ll T$ .

Being guided by the dipole character of radiation, where the rate of a radiative transition is proportional to the square of the matrix element of the dipole moment operator between transition states, one can obtain the following expression for the rate of a vibrational-rotational transition

$$w(v, J \rightarrow v', J') = \frac{1}{\tau_{vv'}} \cdot |\langle JM|\mathbf{n}|J'M'\rangle|^2 = \frac{W(J'M')}{\tau_{vv'}} \quad (4.1.14)$$

Here  $\tau_{vv'}$  is the radiative time for transition between indicated vibrational states,  $\mathbf{n}$  is the unit vector directed along a molecular vibrations,  $J, M; J', M'$  are rotational momenta and their projections onto a given axis for the initial and final transition states correspondingly. This matrix element in formula (4.1.14) results from summation of the initial momentum and unit photon momentum into the momentum of a final state [3–5] and is expressed through the Clebsch-Gordan coefficient. Values of Clebsch-Gordan coefficients which are responsible for a radiative transition are given in Table 4.2 [6].

Values of the Clebsch-Gordan coefficients leads to the selection rules for radiative rotational transitions, and according to them the following transitions are possible

**Table 4.3** Probabilities of radiative vibrational-rotational transitions in a given rotational state

Branch	Transition energy	$W_{\perp}$	$W_{\parallel}$
P ( $J' = J - 1$ )	$\hbar\omega_o + 2B(J + 1)$	$\frac{(J+1)(J+2)+m^2}{2(J+1)(2J+1)}$	$\frac{2J+3}{3(2J+1)}$
Q ( $J' = J$ )	$\hbar\omega_o$	$\frac{J(J+1)-m^2}{2J(J+1)}$	$\frac{1}{3}$
R ( $J' = J + 1$ )	$\hbar\omega_o - 2BJ$	$\frac{J(J-1)+m^2}{2J(2J+1)}$	$\frac{2J-1}{3(2J+1)}$

$$\begin{aligned}
 \Delta\varepsilon &= \hbar\omega_o - 2BJ, \quad J' = J - 1 \longrightarrow P\text{-band,} \\
 \Delta\varepsilon &= \hbar\omega_o, \quad J' = J \longrightarrow Q\text{-band,} \\
 \Delta\varepsilon &= \hbar\omega_o - 2B(J + 1), \quad J' = J + 1 \longrightarrow R\text{-band,}
 \end{aligned}
 \tag{4.1.15}$$

The probability of a given final rotational state depends on relative directions of vibrational and rotational axes. These probabilities for their identical directions  $W_{\parallel}$  and their perpendicular directions  $W_{\perp}$  are given in Table 4.3 depending on rotational quantum numbers  $Jm$ .

Note that for an antisymmetric vibrational state, as well as for a diatomic molecule, the probability of a given final rotational state is  $W_{\parallel}$ , whereas for torsion vibrations it is equal to  $(W_{\parallel} + W_{\perp})/2$ . Averaging these probabilities over the momentum projection  $m$  onto a rotational axis which varies from 0 to  $J$ , we use that the average square of the momentum projection is equal

$$\overline{m^2} = \frac{J(J + 1)}{3}
 \tag{4.1.16}$$

This averaging leads to the following expression for each band

$$\overline{W_P} = \frac{2J + 3}{3(2J + 1)}, \quad \overline{W_Q} = \frac{1}{3}, \quad \overline{W_R} = \frac{2J - 1}{3(2J + 1)}
 \tag{4.1.17}$$

where indices indicate a branch. In the limit of large  $j$  these probabilities become identical and are equal to  $1/3$ . Being guided by large rotational momenta  $j$ , we below take the probability of each branch to be  $1/3$ . Thus, the analysis of spectroscopic properties of  $\text{CO}_2$  molecule allows us to select vibrational-rotational radiative transitions in linear molecules which compose the molecular spectrum and determine the rates of these transitions.

### 4.1.3 Radiative Properties of $\text{CO}_2$ Molecule

In continuation of the analysis of molecular radiative properties, we consider below the carbon dioxide molecule from this standpoint. The study of radiative properties of the carbon dioxide molecule is of importance twofold. On the one hand, this is

a symmetric linear molecule; therefore it is a simple example for demonstration of the general positions in radiation of molecular gases. On the other hand, carbon dioxide is of importance for the greenhouse phenomenon in atmosphere of the Earth and Venus. Therefore, radiative parameters of  $\text{CO}_2$  molecules are required for the analysis of these phenomena. In consideration vibrational-rotational transitions of  $\text{CO}_2$  molecules, we use the Born-Oppenheimer approximation [7] which account for a fast reaction of an electron subsystem to displacements of nuclei. As a result, molecular oscillations take place in a potential field which is formed by electrons at a given configuration of nuclei [8, 9].

Being guided by lower excitations which are associated with vibrational and rotational degrees of freedom for this molecule, we are restricted by the ground electron state with zero spin. Then the distribution of the electron number density is characterized by the axial symmetry, i.e. the electron state of this molecule is conserved as a result of turn around the molecular axis at any angle. Correspondingly, the electron state is conserved at electron reflection with respect of any plane which passes through the molecular axis.

Restricting by nuclear positions near the minimum of the potential energy surface, one can reduce the nuclear motion to their vibrations as harmonic oscillations. In the case of triatomic molecules, where three atoms are located in one line, there are 9 degrees of freedom which include three translation ones, two rotational ones for the molecule axis and four vibrational degrees of freedom. Four types of oscillations for  $\text{CO}_2$  molecules which include the symmetric oscillation, where a distance between each oxygen atom and a central carbon atom are kept identical during this vibration, and the antisymmetric oscillation, where the distance between oxygen atoms is not changed in these oscillations along the molecular axis. In the course of the torsion oscillation (or the deformation vibration) the carbon atom moves perpendicular to the molecular axis, and because of two directions perpendicular to the molecular axis, two torsion oscillations are realized. Because the dipole moment operator is antisymmetric for molecular reflection with respect to the plane, which is perpendicular to the molecular axis and passes through the carbon nucleus, the radiative transitions involving vibrational states do not include symmetric oscillations. Only a change in antisymmetric and torsion vibrational states can lead to radiative dipole transitions.

Let the molecular axis be directed along the axis  $z$ , so that torsion oscillations occur in directions  $x$  and  $y$ . In particular, in the case of excitation of the lower torsion vibration one can compose two vibrations such that the wave function of eigen oscillation are proportional to  $\exp(i\varphi)$  and  $\exp(-i\varphi)$ , where  $\varphi$  is the angle in the plane  $xy$  with respect to the axis  $x$ . In this interpretation we present torsion vibrations and rotations in the plane  $xy$ . In the case of the inversion transformation  $x \leftrightarrow -x$ ,  $y \leftrightarrow -y$ ,  $z \leftrightarrow -z$  the torsion states are separated in even and odd substates in accordance with the property of the eigenfunction to conserve or change its sign. Namely, the torsion vibrations are even with respect to the inversion transformation are odd for the odd number of torsion vibrational quanta, and they are even, if a number of torsion excitations for this state is even.

Note that the abundance of the isotope  $^{12}\text{C}$  in nature is 98.9%, and the abundance of the isotope  $^{16}\text{O}$  is 99.76%. The nuclear spin of each of these isotopes is zero, so that practically all the  $\text{CO}_2$  molecules in nature contain nuclei with zero spin. This leads to the symmetry for molecular reflection with respect to the plane which is perpendicular to the molecular axis and passes through the carbon atom. This operation is analogous to exchange by oxygen molecules which are identical because of zero nuclear spin; in addition it corresponds to reflection of the carbon atom with respect to the symmetry plane. Since the nuclear spin of the carbon atom is zero, and its electron state is conserved at this operation, we obtain the total conservation of the state of the  $^{12}\text{C}^{16}\text{O}_2$  as a result of the above reflection.

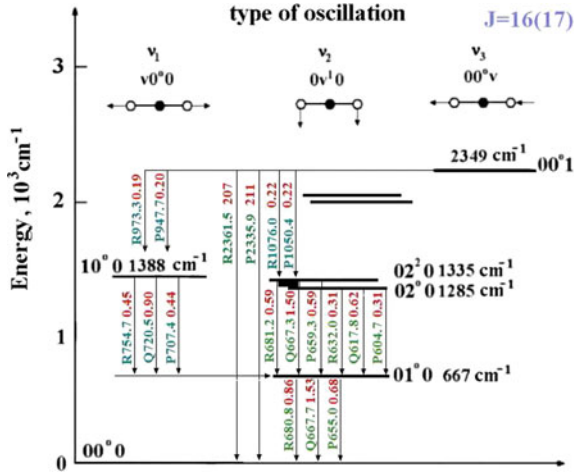
Since the electron, vibrational and rotational degrees of freedom are separated, the total wave function of this molecule is the product of the electron, vibrational and rotational wave functions. Because of the symmetry of the electron state of this molecule both for inversion and reflection with respect to the symmetry plane, the vibrational and rotational states must have a certain symmetry. Because the rotational wave function for the state with the rotation momentum  $J$  of the molecule changes as  $(-1)^J$  as a result of inversion [4], this gives the rotational states which can be realized for a given vibrational state. Indeed, the wave functions of symmetric and antisymmetric oscillations along the molecular axis are not changed as a result of the inversion operation, whereas due to torsion oscillations, the vibrational wave function is conserved for an even number of torsion quantum number and changes its sign for odd values of the torsion quantum number.

Thus, we obtain that in the case of the even value of the torsion quantum number, only rotational states with even values of the rotational momenta  $J$  exist, while in the case of an odd torsion quantum number, there are rotational states with odd  $J$  only realized. The  $\text{CO}_2$  molecule is symmetric for reflection with respect to the symmetry plane, and its rotational states are separated into the even and odd states. These states are connected with the rotational momentum. Namely, the wave functions of states with even rotational numbers are conserved at the indicated operation, but the wave functions of rotational states with odd values of rotational numbers change a sign at this operation [4].

Figure 4.3 contains the spectrum for radiative vibrational-rotational transitions of the  $\text{CO}_2$  molecule. This information is taken from the HITRAN data bank, relates to the temperature  $T = 296$  K, and includes radiative transitions from the states with the rotational number  $J = 16$  for even vibrational states and  $J = 17$  for odd ones. The distribution function of  $\text{CO}_2$  molecules over rotational states has the maximum at these rotational numbers for the used gas temperature  $T = 296$  K. Three atoms of the  $\text{CO}_2$  molecule lie on a line, and three types of oscillations are as follows:  $\nu_1$  is the symmetric oscillation,  $\nu_2$  is the torsion one, and  $\nu_3$  is the antisymmetric oscillation. We are restricted ourselves by lower vibrational states which give a remarkable contribution to the absorption coefficient due to vibrational-rotational transitions of the  $\text{CO}_2$  molecule. Therefore such excited vibrational states are excluded from Fig. 4.3.

Let us formulate the selection rules for the carbon dioxide molecule being guided by those for diatomic molecules. For the strongest vibrational radiative transitions,





**Fig. 4.3** Absorption spectrum of the carbon dioxide molecule and its radiative parameters according to HITRAN data bank [10, 11]. The energies of radiative transitions are expressed in  $\text{cm}^{-1}$  and are given in green; letters  $P$ ,  $Q$  and  $R$  correspond to  $P$ ,  $Q$  and  $R$ -branches of the rotational transitions correspondingly. Values of the Einstein coefficient are presented in red; they are expressed in  $\text{s}^{-1}$ . The initial rotational state for all the radiative transitions correspond to the rotational number  $J = 16$ , if the initial state admits only even rotational momenta, and  $J = 17$  for odd rotational momenta in the initial state

the change of the vibrational quantum number is one as well as in the model of the harmonic oscillator. Note that in the case under consideration we assume vibrational excitation to be not strong, so that vibrational states of different types are separated, i.e. the total vibrational wave function is a product of wave functions for vibrational states of a different type. Evidently, if the torsion vibrational state is not changed at the radiative transitions, the selective rule is the same, as in the case of diatomic molecules. Other selection rules are in the case where the torsion vibration state is changed.

We now analyze vibrational states with a lower excited state of the torsion excitation. From two torsion states with oscillations in two perpendicular directions one can combine two rotational states around the molecular axis, and formally one can present the total molecular momentum as a sum of rotation of the molecular axis with a momentum  $J$  and torsion rotation which momentum we take to be  $1/2$  because of two rotational states. Correspondingly, the wave function  $\Psi$  of total rotations can be constructed from the wave function  $\psi$  of axial rotation, and wave function  $\varphi$  for torsion rotation. Summarizing rotation momenta, one can formally represent the total wave functions of rotations as

$$\Psi_{J+1/2} = \frac{1}{\sqrt{2}} (\psi_J \varphi_{1/2} + \psi_{J+1} \varphi_{-1/2}), \quad \Psi_{J-1/2} = \frac{1}{\sqrt{2}} (\psi_J \varphi_{-1/2} + \psi_{J-1} \varphi_{1/2}), \quad (4.1.18)$$

It should be noted that  $J$ , as the rotational number of the initial state, is an even number, at which this state is stable. Correspondingly, at torsion excitation the states with rotational numbers  $J + 1$  and  $J - 1/2$  are stable, whereas the state with rotational number  $J$  is unstable, as it follows from the symmetry of the total wave function if three atoms which are arrayed along a line [4]. If the carbon atom deviates from the line, this symmetry requirement disappears. Hence, the wave function with the rotational number  $J$  is zero only at the nuclear configuration if they form one line. As a unstable state, this state decays subsequently, but it is present in the absorption spectrum along with stable states.

We now determine the probabilities  $W_P$ ,  $W_Q$ ,  $W_R$  for realization the  $P$ ,  $Q$  and  $R$ -branches of radiation in the case if the torsion vibrational state is changed at this transition. Assuming that the states with total rotational numbers  $J + 1/2$  and  $J - 1/2$  are formed with the equal probability, we find on the basis of the wave functions (4.1.18) the probabilities of realization of  $P$ ,  $Q$  and  $R$  branches are equal correspondingly

$$W_P = \frac{1}{4}, \quad W_Q = \frac{1}{2}, \quad W_R = \frac{1}{4}, \quad (4.1.19)$$

and the relation between the Einstein coefficients  $A$  for these branches is as follows

$$A_Q = 2A_P = 2A_R \quad (4.1.20)$$

#### 4.1.4 Spectroscopic Databases

Analyzing processes in molecular gases, we use parameters of radiative transitions in molecular gases for the HITRAN data bank. Therefore we use partially notations of this data bank for molecular gases. Along with this, other data banks exist where information for various aspects of spectroscopy is given. We represent below a list of such data banks along with the HITRAN one [11].

*Millimeter and Submillimeter Molecular Spectroscopy Catalog*, Jet Propulsion Laboratory, USA

*The Cologne Database for Molecular Spectroscopy (CDMS)*, Universität zu Köln, Germany

*GEISA Spectroscopic Database*, Laboratoire de Metrologie Dynamique, France

*PNNL Vapor Phase Infrared Spectral Library*, Pacific Northwest National Laboratory, USA

*ExoMol*, Molecular line lists for exoplanet and cool star atmospheres, University College London, UK

*Ames Molecular Spectroscopic Data For Astrophysical and Atmospheric Studies*, NASA Ames, USA

*TheoReTs*, Internet accessible information system "Theoretical Reims-Tomsk Spectral data, University de Reims, France and Institute of Atmospheric Optics, Russia

*Spectroscopy and Molecular Properties of Ozone*. University de Reims, France and Institute of Atmospheric Optics, Russia

*NIST Wavenumber Calibration Tables* from Heterodyne Frequency Measurements, National Institute of Standards and Technology, USA NIST Atomic Spectra Database, National Institute of Standards and Technology, USA

*CHIANTI*, An Atomic Database for Spectroscopic Diagnostics of Astrophysical Plasmas, George Mason University (USA), University of Michigan (USA), University of Cambridge (UK).

## 4.2 Absorption of Infrared Radiation in Gas of Linear Molecules

### 4.2.1 Infrared Radiation of Molecular Gas

We above have considered radiative transitions between discrete atom states, where the spectrum of absorption or emission is characterized by separate spectral lines. Each line can be splitted in a multiplet due to fine and superfine interactions inside an atom or atomic ion, but the frequency width of each multiplet is relatively small. This means that the spectrum of atoms or atomic ions consists of separate spectral lines which can be splitted in a multiplet, but at frequencies between neighboring spectral lines or multiplets it is zero. In the case of radiative transitions between electronic states of molecules, vibrational and rotational spectra apply with the electron one. As a result, an absorption line in the atomic case is transformed in an absorption band for molecular particles with an oscillating spectrum structure as a frequency function. Because of a high frequency width of an absorption band, neighboring bands may be overlapped, so that the physical picture of radiation interaction with molecular particles differs from that in the case of atoms and ions.

In order to consider the nature of vibrational-rotational transitions from the general positions of molecular spectroscopy [12–16], we below analyze the character of of absorption and emission of molecular gases. Moreover, we consider radiative transitions without change of the electron state; first we are restricted ourself by one vibrational transition. Next, for simplicity, we consider the case of linear molecules. The absorption of a molecular gas corresponds to the infrared spectrum range, and due to selection rules radiative transitions are accompanied by change of vibrational  $v$  and rotational  $J$  quantum numbers in the following way  $v, J \rightarrow v', J'$  with  $v' = v \pm 1$ ,  $J' = J, J \pm 1$ . Thus, according to selection rules  $Q$ -branch correspond to the rotational transition  $J \rightarrow J$ ,  $P$ -branch refers to the transition  $J \rightarrow J + 1$ , and  $R$ -branch relates to the rotational transition  $J \rightarrow J - 1$ . Note that in the case of a diatomic molecule, where vibrations take place along the molecular axis,  $Q$ -branch is absent for rotational transitions.

The energy of the rotational state of the molecule  $E_J$  is [4]

$$E_J = BJ(J + 1), \quad (4.2.1)$$

Here  $B = \hbar^2/2\mu$  is the rotational constant, and the energy of the rotational state is equal  $\hbar\omega_J = \hbar\omega_o - 2BJ$  for  $P$ -branch with the transition  $J \rightarrow J + 1$  it is equal  $\hbar\omega_J = \hbar\omega_o - 2BJ$ , and for  $R$ -branch with the transition  $J \rightarrow J - 1$ , the energy of the transition is  $\hbar\omega_J = \hbar\omega_o + 2B(J + 1)$ , where  $\hbar\omega_o$  is the energy difference for vibrational states of the transition.

We now consider radiative properties of a molecular gas where broadening of spectral lines is determined by collisions with molecules of a buffer gas where radiating molecules are located. Note the difference for broadening of spectral lines for atoms and molecules. In the atomic case, the interaction potential of a radiating atom in the upper state of transition with a buffer gas atom exceeds significantly that for the lower transition state; therefore broadening of an atom spectral line for the impact and quasistatic theory is determined by interaction in the upper transition state. In the case of molecular radiation, parameters of interaction of a radiating molecule and a buffer gas atom in the upper and lower states of the radiative transition are nearby, i.e. the difference of interaction potentials for the upper and lower states of the radiative transition is small.

Let us analyze this effect for molecules of  $\text{CO}_2$  in a parent gas approximating the interaction potential of two  $\text{CO}_2$  molecules at large distances between them by formula (2.1.41)  $U(R) = -C_6/R^6$ . Taking the difference of the interaction potentials for the upper and lower states of the radiative vibration transition as  $\Delta U(R) = -\Delta C_6/R^6$ , one can obtain instead of formula (2.1.43) for the width of the spectral line

$$\frac{\nu}{N_b} = 7.2 \left( \frac{2T}{\mu} \right)^{3/10} \left( \frac{\Delta C_6}{\hbar} \right)^{2/5} \quad (4.2.2)$$

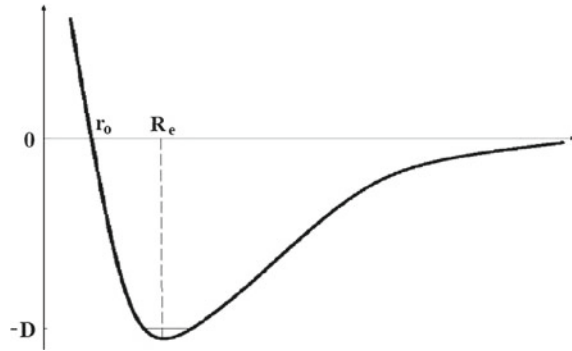
Let us use the experimental value of the width of the spectral line for the vibrational transition  $001 \rightarrow 000$  at  $667 \text{ cm}^{-1}$  that is equal according to measurements  $\nu = 0.16 \text{ cm}^{-1}$  [17–20]. Then formula (4.2.2) gives for the difference  $\Delta C_6 = 32e^2 a_o^5$ , whereas its value is  $C_6 = 118e^2 a_o^5$  [1]. This shows the degree of the difference of the interaction potentials for neighboring molecular vibrational states.

One more peculiarity of spectral lines due to vibrational transitions is their restricted width for the collision mechanism of broadening. Indeed, at wings of a spectral line the distribution function  $a_\omega$  according to formula (2.1.40) has the form

$$a_\omega = \frac{\nu}{2\pi (\omega - \omega_o)^2} \quad (4.2.3)$$

The broadening is determined by collisions with buffer gas atoms or molecules, and  $\omega_o$  is the frequency at the line center. In derivation of formula (2.1.40) for collision broadening of the spectral line we assume a collision time to be zero, and then the distribution function (4.2.3) is spreading up to infinite frequency. But according to the nature of this effect, it is necessary to restrict frequencies in this formula

**Fig. 4.4** Parameters of the Lennard-Jones interaction potential for two molecules



by  $|\omega - \omega_0| \sim 1/\tau_c$ , where  $\tau_c$  is a duration time of the collision event. We below estimate this time for collisions of a radiating  $\text{CO}_2$  molecule which is located in a parent gas, approximating, for simplicity, the interaction potential of two molecules of carbon dioxide by the Lennard-Jones interaction potential [21, 22]

$$U(R) = D \left[ 2 \left( \frac{R_e}{R} \right)^6 - \left( \frac{R_e}{R} \right)^{12} \right], \quad (4.2.4)$$

Here  $D$  is the depth of the potential well for the interaction of two molecules,  $R_e$  is the equilibrium distance between molecules, which corresponds to a minimum of the interaction potential, and its parameters are given in Fig.4.4. Though the spherically symmetric interaction potential is a crude approximation for interaction of carbon dioxide molecules, but this allows us to describe simply the effect under consideration. One can determine parameters of the interaction potential between two  $\text{CO}_2$  molecules on the basis of the similarity law by comparison the interaction parameters of carbon dioxide molecules and inert gas atoms. Indeed, the scaling law for inert gases [23, 24] allows one to connect critical parameters of inert gases and carbon dioxide, and also their parameters near the triple point with parameters of the pair interaction potential inside these systems. In this manner, one can determine parameters of the pair interaction potential of molecules in formula (4.2.4), which in the case of carbon dioxide molecules gives  $D = (38 \pm 7)$  meV and  $R_e = 0.32$  nm. As is seen, the accuracy of this operation is restricted. This comparison allows us to determine the van der Waals interaction constant  $C_6 = 2DR_e^6 \approx 140e^2a_0^5$  on the basis of the above scaling law, using parameters of inert gases. This exceeds the calculated value [1] by 20%.

One can define a typical collision time for two molecules of carbon dioxide  $\tau_c$  as a time of approach of slow molecules from the distance  $R_e$  at the minimum interaction potential of molecules to the distance  $r_0 = R_e/2^{1/6}$  that corresponds to the potential wall for slow molecules at zero orbital angular momentum (see Fig.4.3), which is equal to

$$\frac{1}{\tau_c} \equiv \Delta\omega = \frac{10}{R_e} \cdot \sqrt{\frac{2D}{m}}, \quad (4.2.5)$$

where  $m$  is the mass of the carbon dioxide molecule. Hence we obtain the following estimate for the wing width of the absorption band of carbon dioxide molecules in carbon dioxide  $\Delta\omega \approx 70 \text{ cm}^{-1}$ . This fact restricts the flux of IR radiation emitted by carbon dioxide due to spectral line wings.

## 4.2.2 Vibrational-Rotational Radiative Transitions for Diatomic Molecules

We now determine the absorption coefficient  $k_\omega$  due to optically active diatomic molecules under conditions of the thermodynamic equilibrium between vibrational and rotational molecular states. According to the selection rule, the strongest transition for a diatomic molecule within the framework of the harmonic oscillator model is  $v \rightarrow v + 1$  in the process of the photon absorption. Separating vibrational and rotational states, one can obtain the number density of molecules in the lower state

$$N_i = CN_v(2J + 1) \exp\left[-\frac{BJ(J + 1)}{T}\right],$$

Here the normalization coefficient  $C$  under the criterion  $B \ll T$  is equal  $C = B/T$ , and  $N_v$  is the number density of molecules in the lower vibrational state of the radiation transition; it is described by vibrational and rotational states with quantum numbers  $vJ$ . We thus have for the absorption coefficient  $N_v = \sum_i N_i$  where  $N_i$  is the number density of molecules in the lower transition state, and  $g_i = 2J + 1$  because the radiative transition takes place from a rotational state with the quantum number  $J$ . Under these conditions formula (2.2.28) gives for the absorption coefficient

$$k_\omega = N_v A_{ij} g_j \exp\left(-\frac{E_i}{T}\right) \left(\frac{\pi c}{\omega}\right)^2 a_\omega \frac{B}{T} \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \quad (4.2.6)$$

where  $g_j = 2J' + 1$  is the statistical weight for the final state  $j$  with the rotational quantum number  $J'$ ,  $E_i = BJ(J + 1)$  is the rotational energy of the initial state  $i$ .

In order to reduce this expression to parameters of the HITRAN data bank which data are used below, we introduce the spectral line intensity as

$$S_{ij} = \int \sigma_\omega d\nu = \int \frac{k_\omega}{N_v} \frac{d\omega}{2\pi c}, \quad (4.2.7)$$

where the cross section of absorption is introduced as  $\sigma_\omega \equiv \sigma_{ij} = k_\omega/N_v$ , and the value  $\nu$  is the reciprocal wavelength of radiation  $\nu = 1/\lambda = \omega/(2\pi c)$ . Using the normalization condition (2.1.1), one can obtain

$$S(\omega) = A_{ij} g_j \frac{B}{T} \exp\left(-\frac{E_i}{T}\right) \left(\frac{\pi c}{2\omega^2}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] \quad (4.2.8)$$

The spectral line intensity is a convenient characteristic of vibrational-rotational transitions because this value does not depend on broadening of corresponding spectral lines.

It is necessary to compare this expression with that [25] given by the HITRAN data bank. Taking into account that the value  $S_{ij}$  has the dimensionality of length and accepting the spectroscopy unit  $\text{cm}^{-1}$  and thermal unit  $K$  as the energy units, one can present the spectral line unit of the HITRAN data bank [25] in the form

$$S_{ij} = \frac{I_a}{I_o} \frac{A_{ij}}{8\pi c \nu_{ij}^2} \frac{g_i}{Q(T)} \exp\left(-\frac{E_i}{T}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] \quad (4.2.9)$$

In rewriting the HITRAN expression for the spectral line intensity, we accept that the units  $\text{cm}^{-1}$  and  $K$  to be the energy units. Next, the inertia moment is  $I_a = \mu r_o^2 = \hbar^2/(2B)$  ( $\mu$  is the reduced mass of nuclei,  $r_o$  is the equilibrium distance between them), the atomic value of this dimensionality is  $I_o = m_e a_o^2$  ( $a_o$  is the Bohr radius), the reciprocal wavelength for this radiative transition  $\nu_{ji}$  is expressed through the frequency  $\omega$  as  $\nu_{ji} = \omega/2\pi c$ ; in addition, we consider the frequency  $\omega$  as a continuous variable. Next,  $E_i = BJ(J+1)$  is the rotational energy, and  $Q(T) = \sum_k g_k \exp(-E_k/T)$  is the partition function. Being guided by real conditions, where  $T \gg B$ , and only the lower vibrational state gives the contribution to the partition function, we replace the sum by integral and obtain  $Q(T) = T/B$ . Then formulas (4.2.8) and (4.2.9) coincide with each other. Below, considering the frequency  $\omega$  as a continuous variable and being guided by large  $J$ , we have

$$g_j = 2J + 1 = \frac{\hbar(\omega - \omega_o)}{B}$$

This allows us to rewrite formula (4.2.8) in the form

$$S(\omega) = A_{ij} \frac{\lambda^2}{8\pi c} \frac{\hbar|\omega - \omega_o|}{T} \exp\left(-\frac{\hbar^2|\omega - \omega_o|^2}{4BT}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \quad (4.2.10)$$

where  $\lambda = 2\pi c/\omega$  is the radiation wavelength,  $\hbar\omega_o$  is the energy difference between energies of vibrational states of this transition. This expression relates both to  $P$ -branch and  $R$ -branch. We use this expression below in determination of the spectral line intensity.

Note that we consider above the frequency  $\omega$  as a continuous variable. Then the spectral line intensity has the maximum at  $\hbar\omega_{\max} = 2\sqrt{BT}$ , and the maximum value of this quantity is equal

$$S_{\max} = A(J_{\max}) \frac{\lambda_m^2}{8\pi c \sqrt{e}} \sqrt{\frac{2B}{T}} \left[ 1 - \exp\left(-\frac{\hbar\omega}{T}\right) \right], \quad (4.2.11)$$

where  $J_{\max}$  is the rotational momentum,  $\lambda_m$  is the radiation wavelength. Correspondingly, one can express the spectral line intensity  $S(\omega)$  through its maximum value  $S_{\max}$  as

$$S(\omega) = \sqrt{2e} S_{\max} \frac{\hbar|\omega - \omega_o|}{2\sqrt{BT}} \exp\left(-\frac{\hbar^2|\omega - \omega_o|^2}{4BT}\right) \quad (4.2.12)$$

One can compare this value with that from the HITRAN data bank [11] in the case of CO-molecules. At the temperature  $T = 296$  K and for the rotational constant of the CO molecule  $B = 1.93 \text{ cm}^{-1}$ , the maximum of the spectral line intensity corresponds to  $J_{\max} = 7$ ; the photon energy is  $\hbar\omega_7 = 2116 \text{ cm}^{-1}$  for  $P$ -branch, and  $\hbar\omega_7 = 2173 \text{ cm}^{-1}$  for  $R$ -branch. Taking values of the Einstein coefficient  $A_7 = 18.4 \text{ cm}^{-1}$  and  $A_7 = 17.5 \text{ cm}^{-1}$  for these cases, we have the values of the spectral line intensity  $S_7 = 3.87 \cdot 10^{-19} \text{ cm}$  for  $P$ -branch and  $S_7 = 4.56 \cdot 10^{-19} \text{ cm}$  for  $R$ -branch according to data of HITRAN bank [11]. Formula (4.2.11) gives for these cases  $S_7 = 4.2 \cdot 10^{-19} \text{ cm}$  for  $P$ -branch and  $S_7 = 3.8 \cdot 10^{-19} \text{ cm}$  for  $R$ -branch. As is seen, agreement between these results take place with the accuracy of 20%.

### 4.2.3 Absorption Coefficient for Gas of Diatomic Molecules

We below construct the absorption coefficient  $k_\omega$  for a certain band of a radiative vibrational transition of a linear molecule in the case of collision broadening of spectral lines. Then the lower and upper transition states of Fig. 1.4 are characterized by the vibrational  $v$  and rotational  $J$  quantum numbers which relate to the number of vibrational or rotational states. The selection rules extract a restricted number of transitions, and the strongest transitions for absorption of radiation are  $v, J \rightarrow v + 1, J + 1$  for  $P$ -branch and  $v, J \rightarrow v + 1, J - 1$  for  $R$ -branch. The absorption coefficient  $k_\omega$  accounted for a transition between two states is given by formula (2.2.28) and is equal

$$k_\omega = A_{ij} N_v \frac{\lambda^2}{4} \frac{\hbar|\omega - \omega_o|}{T} a_\omega \exp\left[-\frac{\hbar^2(\omega - \omega_o)^2}{4BT}\right] \left[ 1 - \exp\left(-\frac{\hbar\omega}{T}\right) \right], \quad (4.2.13)$$

where  $\lambda$  is the radiation wavelength. We above separate vibrational and rotational states, so that in this formula  $N_v$  is the number density of molecules in the lower vibrational state  $v$  for the radiative transition  $v \rightarrow v'$ , and indices  $i$  and  $j$  correspond to the initial  $J$  and final  $J'$  rotational states,  $\omega$  is the transition frequency,  $\hbar\omega_o$  is the energy difference for vibrational transition states,  $c$  is the speed of light,  $A_{ij}$  is the first Einstein coefficient which depends weakly on the rotational number; it is



taken into account a large number of rotational states which determine the absorption coefficient, and the summation in formula (4.2.13) is made over rotational states. We assume molecules in rotational and vibrational states to be under thermodynamic equilibrium with the temperature  $T$ . According to the selection rule, the vibrational number is changed by one within the framework of the harmonic oscillator for molecular vibrations. The criterion  $J \gg 1$  allows one also to neglect interaction of nuclear rotation with electron momenta, i.e.,  $J = K$ , where  $K$  is the total molecular moment.

Formula (4.2.13) joins transitions for  $P$ -branch with  $\omega \geq \omega_0$  and  $R$ -branch with  $\omega \leq \omega_0$ . The variation energy  $\hbar\omega_J$  for a given vibrational transition and the initial rotational momentum  $J$  of the molecule is given by

$$\hbar\omega_J = \hbar\omega_0 - B \pm B(2J + 1), \quad (4.2.14)$$

where the sign minus relates to  $P$  absorption branch, sign plus corresponds to  $R$ -branch. From this it follows for  $P$  and  $R$  branches  $\hbar\omega_J = \hbar\omega_0 - B \pm 2BJ$  for large  $J \gg 1$  that we use below. As is seen, the energy difference between neighboring rotational states is constant that corresponds to the Elsasser model [26], and this difference is  $2B$ . The photon distribution function  $a_\omega$  for a certain transition has the Lorentz shape (2.1.4); in the case of the collision mechanism of broadening of spectral lines which is of the most interesting, the photon distribution function has the form

$$a_\omega = \sum_J \frac{\nu_J}{2\pi [(\omega - \omega_0 - \omega_J)^2 + (\frac{\nu_J}{2})^2]}, \quad (4.2.15)$$

where the width  $\nu_J$  of spectral lines depends weakly on  $J$ .

The absorption coefficient is a harmonic function of the frequency (or almost harmonic one, if we take into account a weak frequency dependence of parameters in formulas (4.2.13) and (4.2.15)), and the period of oscillations is  $2B/\hbar$ . We now determine the average absorption coefficient averaged over frequencies. Accounting for the normalization condition (2.1.1) and the distance between neighboring resonance frequencies to be  $2B/\hbar$ , we obtain on the basis of formula (2.2.28) for the average absorption coefficient  $\chi(\omega)$  which is expressed through the spectral line intensity  $S(\omega)$  defined by formula (4.2.7), as

$$\chi(\omega) = \overline{k_\omega} \equiv \frac{\hbar}{2B} \int_{-\infty}^{\infty} k_\omega d\omega = \frac{2\hbar N_v \pi c}{d} S(\omega) = N_v \lambda_d S(\omega), \quad (4.2.16)$$

Here  $\lambda_d = 2\pi c \hbar / d$  is the wavelength for a photon of an energy  $d$ , which is in turn the difference of neighboring energy levels, and in the case of diatomic molecules is equal to  $d = 2B$ .

Finally, the value of this quantity in the case of optically active diatomic molecules is given by

$$\chi(\omega) = A_{ij} N_v \frac{\lambda^2 \hbar^2 |\omega - \omega_o|}{8 BT} \exp\left(-\frac{\hbar^2(\omega - \omega_o)^2}{4BT}\right) \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] \quad (4.2.17)$$

A general form of the absorption coefficient is

$$k_\omega = \chi(\omega)\varphi(\omega), \quad \int_{-\infty}^{\infty} \varphi(\omega) d\omega = 1 \quad (4.2.18)$$

and the function  $\varphi(\omega)$  takes into account the oscillation character of the absorption coefficient. One can rewrite also the connection between the spectral line intensity and average absorption coefficient on the basis of formulas (4.2.7) and (4.2.16)

$$S(\omega) = \frac{\chi(\omega)d}{N_v \cdot 2\pi c}, \quad (4.2.19)$$

Here  $d$  is the energy difference for neighboring transitions, and for diatomic molecules we have  $d = 2B$ .

In order to determine  $\varphi(\omega)$ , we use the Mittag-Leffler theorem, that takes the form [27]

$$\sum_{k=-\infty}^{\infty} [(x-k)^2 + y^2]^{-1} = \frac{\pi \sinh 2\pi y}{y(\cosh 2\pi y - \cos 2\pi x)} \quad (4.2.20)$$

Taking now  $x = \hbar(\omega - \omega_o)/B$  and  $y = \hbar\nu/4B$ , one can present the absorption coefficient  $k_\omega$  into a given absorption band in the form (4.2.18) (for example, [28–30]) with

$$\varphi_i(\omega) = \sinh \frac{\pi \hbar\nu}{2B} \left[ \cosh \frac{\pi \hbar\nu}{2B} - \cos \frac{\pi \hbar(\omega - \omega_i)}{B} \right]^{-1}, \quad (4.2.21)$$

Thus, we have that the absorption coefficient is an oscillation function of the frequency; according to formulas (4.2.18) and (4.2.21), the ratio of the neighboring maximum  $k_{\max}$  and minimum  $k_{\min}$  values of the absorption coefficient is

$$\frac{k_{\max}}{k_{\min}} = \frac{\cosh \frac{\pi \hbar\nu}{2B} + 1}{\cosh \frac{\pi \hbar\nu}{2B} - 1}, \quad (4.2.22)$$

In the limit of a low pressure, if  $\hbar\nu \ll B$ , this formula takes the form

$$\frac{k_{\min}}{k_{\max}} = \left(\frac{\pi \hbar\nu}{4B}\right)^2 \quad (4.2.23)$$

Note that in summarizing over rotational momenta we assume that the photon distribution function  $a_\omega$  depends on the frequency stronger than other functions in

the expression (4.2.13). Let us check it for the distribution function of molecules on energies, i.e. for the dependence of  $\exp[-\hbar^2(\omega - \omega_o)^2/4BT]$ , where the exponent varies through one period  $2B/\hbar$  by the value  $\hbar|\omega - \omega_o|/2T$ . Hence, formulas (4.2.17), (4.2.18) and (4.2.21) hold true if the following criterion is fulfilled

$$\hbar|\omega - \omega_o| \ll 2T \quad (4.2.24)$$

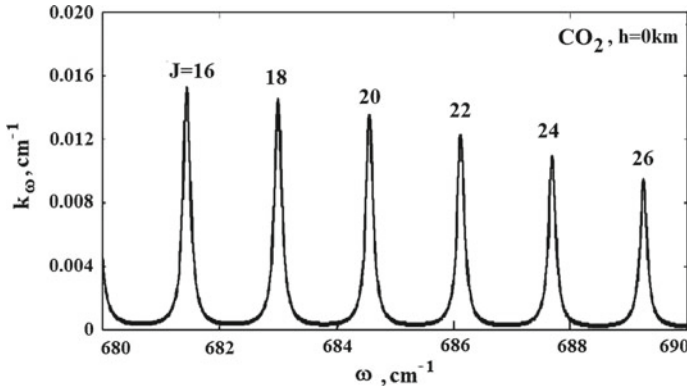
#### 4.2.4 Absorption Coefficient Produced by Carbon Dioxide Molecules

In consideration the spectrum of the CO<sub>2</sub> molecule, we are based on spectroscopy of a diatomic molecule, but take into account peculiarities of CO<sub>2</sub> molecules. Carbon dioxide is an important atmospheric component which gives a remarkable contribution to the greenhouse phenomenon of the Earth's and Venus atmospheres. From another standpoint, this molecule is the linear one, that allows us to analyze spectroscopic properties of gases contained carbon dioxide in the simple manner. For these reasons we analyze spectroscopic properties of a gas with carbon dioxide molecules as one of its components in detail. In evaluating the absorption coefficient  $k_\omega$  of a gas with CO<sub>2</sub> molecules, we use the above expressions (4.2.17), (4.2.16), and (4.2.21) for diatomic molecules. In this analysis we take into account that the CO<sub>2</sub> molecule differs from diatomic molecules as an absorber of infrared radiation, since this molecule has only even values of the rotational momentum  $J$  or only odd ones depending on the parity of the vibration state. For this reason, the energy difference for neighboring vibrational-rotational radiative transitions is equal to  $4B$  instead of  $2B$ , for diatomic molecules, where  $B$  is the molecular rotational constant. In addition, radiative transitions of the  $Q$ -branch are realized in the radiative spectrum of CO<sub>2</sub> molecules if the torsion vibration state changes at this transition.

In the case of a radiative vibrational-rotational transition of  $P$ - or  $R$ -branches, one can use formulas (4.2.17), (4.2.16), and (4.2.21) for the absorption coefficient  $k_\omega$  with the change the rotational constant  $B$  by  $2B$ . Then the absorption coefficient for  $P$  and  $R$ -branches is determined by formula

$$k_\omega^P = A(\omega)N_v \frac{\lambda^2}{4} \frac{\hbar|\omega - \omega_o|}{T} \exp\left[-\frac{\hbar^2(\omega - \omega_o)^2}{4BT}\right] \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] \frac{\sinh \frac{\pi\hbar\nu}{4B}}{\cosh \frac{\pi\hbar\nu}{4B} - \cos \frac{\pi\hbar(\omega - \omega_i)}{2B}}, \quad (4.2.25)$$

where we go from the integer rotational momentum  $J$  to a continuous quantity  $\omega - \omega_o$ ; negative values of  $\hbar(\omega - \omega_o)$  correspond to  $P$ -branch, while positive values of this parameter relate to  $R$ -branch. As is seen, the absorption coefficient as a frequency function has an oscillation structure. Figure 4.5 gives this dependence in a narrow spectrum range for  $P$  branch of the radiative vibrational transition  $00^00 \rightarrow 01^00$  of CO<sub>2</sub> molecules in air at atmospheric pressure. On the basis of formula (4.2.16), this formula may be presented in the form



**Fig. 4.5** Absorption coefficient for  $P$  branch of the  $15\ \mu\text{m}$  vibrational transition  $00^0 0 \rightarrow 01^0 0$  due  $\text{CO}_2$  molecules in air at atmospheric pressure in a narrow range of frequencies

$$k_{\omega}^P = N_v S_{\max} \frac{\lambda_B}{4} \cdot \frac{\hbar|\omega - \omega_o|}{2\sqrt{BT}} \exp\left[-\frac{\hbar^2(\omega - \omega_o)^2}{4BT}\right] \frac{\sinh \frac{\pi\hbar\nu}{4B}}{\cosh \frac{\pi\hbar\nu}{4B} - \cos \frac{\pi\hbar(\omega - \omega_j)}{2B}} \quad (4.2.26)$$

Figure 4.5 demonstrates this dependence for the strongest vibrational transition of  $\text{CO}_2$  molecules in air at room temperature.

Let us consider  $Q$ -branch of radiative transitions which proceed without the change of the rotational momentum  $J$ . In this case the energy of excitation of the rotational state is given by formula (4.2.1)  $E_J = BJ(J + 1)$ , but the transition energy or the photon energy  $\hbar\omega_J$  is given by the formula

$$\hbar\omega_J = \hbar\omega_o - \Delta_J \quad (4.2.27)$$

instead of (4.2.14). In particular, on the basis of HITRAN data [11] we have for this parameter  $\Delta_J$  in the case of the strongest radiative transition  $00^0 0 \rightarrow 01^0 0$  with the energy  $667\ \text{cm}^{-1}$ , the following approximation

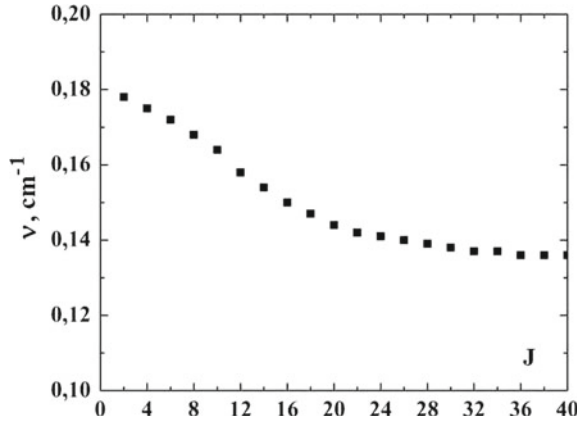
$$\hbar\omega_o = 667.377\ \text{cm}^{-1}, \quad \Delta_J = bJ + cJ^2, \quad b = 2.4 \cdot 10^{-3}\ \text{cm}^{-1}, \quad c = 1.0 \cdot 10^{-3}\ \text{cm}^{-1} \quad (4.2.28)$$

Let us assume that the function  $d\Delta_J/dJ = b + 2cJ$  depends weakly on  $J$  that holds true at large  $J$ . The latter means that with taking into account that only even values of  $J$  are realized, the function  $\varphi(\omega)$  according to formula (4.2.21) has the form

$$\varphi_Q(\omega) = \sinh \frac{\pi\hbar\nu}{2(b + 2cJ)} \left[ \cosh \frac{\pi\hbar\nu}{2(b + 2cJ)} - \cos \frac{\pi\hbar(\omega - \omega_o)}{b + 2cJ} \right]^{-1}, \quad \omega \geq \omega_o, \quad (4.2.29)$$

At moderate value of  $J$ , where the above assumption is not fulfilled,  $\varphi(\omega) = 1$ , whereas at large values of  $J$ , where oscillations in this function are realized, this

**Fig. 4.6** Width of the spectral line for the vibrational transition  $00^00 \rightarrow 01^00$  of the  $\text{CO}_2$  molecule as a function of the rotational momentum  $J$ . This function is the same for  $P$ ,  $Q$  and  $R$ -branches [10]



assumption is fulfilled. The half-width of this spectral line according to HITRAN bank data [11] is nearby to  $\hbar\nu/2 = 0.07 \text{ cm}^{-1}$ ; therefore remarkable oscillations start from the the rotational momenta  $J_o = 16$ , that corresponds to the maximum of the absorption coefficient.

In determination of the absorption coefficient as a function of the photon frequency  $\omega$ , it is necessary to find the connection between the photon frequency and the rotational momentum  $J$ . In order to reduce the expression for the absorption coefficient to the above expressions, we take approximately  $\Delta_J = cJ(J+1)$ , that holds true at large  $J$ . Taking this dependence instead of formula (4.2.14), we have for the distribution function over rotational states  $f_J$  which is normalized to one ( $\int f_J dJ/2 = 1$ ), taking into account that the rotational states with even rotational momenta exist only

$$f_J = \frac{2B(2J+1)}{T} \exp\left[-\frac{BJ(J+1)}{T}\right] = 4\sqrt{\frac{B}{T}} \sqrt{\frac{\omega - \omega_o}{\Delta\omega}} \exp\left[-\frac{\hbar(\omega - \omega_o)}{\Delta\omega}\right], \quad \Delta\omega = \frac{cT}{\hbar B} \quad (4.2.30)$$

This expression relates to positive values  $\omega - \omega_o$ . For the temperature at the Earth's surface  $T = 288 \text{ K}$ , this parameter is equal  $\Delta\omega = 0.051 \text{ cm}^{-1}$ .

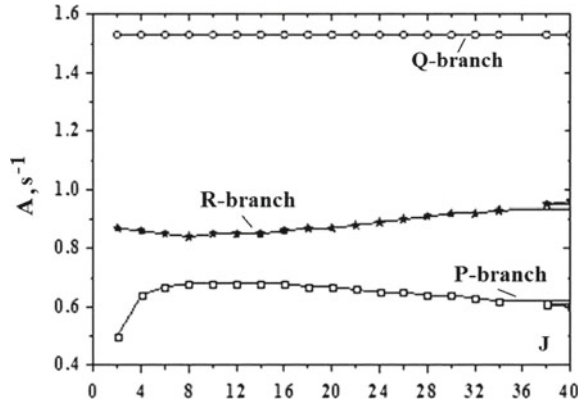
We now determine the absorption coefficient on the basis of formula (2.2.28). Averaging it over oscillations, we obtain for the averaged absorption coefficient

$$\chi_Q(\omega) = A(\omega)N_v \frac{\lambda^2}{2\Delta\omega} \exp\left[-\frac{\hbar(\omega - \omega_o)}{\Delta\omega}\right] \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right], \quad \Delta\omega = cT/(\hbar B) \quad (4.2.31)$$

Correspondingly, the absorption coefficient  $q_\omega$  for  $Q$ -branch of radiative rotational transitions in accordance with formula (4.2.18) is given by

$$q_\omega = A(\omega)N_v \frac{\lambda^2}{2\Delta\omega} \exp\left[-\frac{(\omega - \omega_o)}{\Delta\omega}\right] \left[1 - \exp\left(-\frac{\hbar\omega}{T}\right)\right] \frac{\sinh y}{\cosh y - \cos \frac{y(\omega - \omega_i)}{\nu}}, \quad y = \frac{\pi\hbar\nu}{2(b+2cJ)} \quad (4.2.32)$$

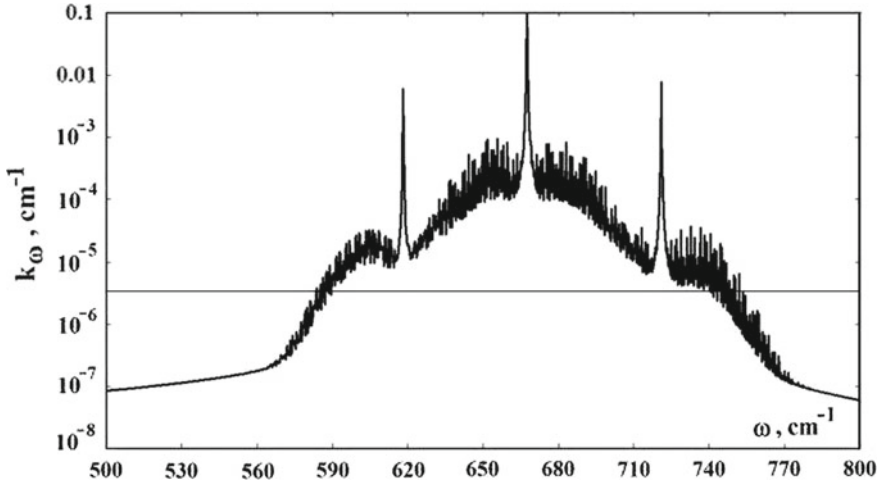
**Fig. 4.7** Dependence of the Einstein coefficient  $A$  for the photon absorption process on the rotational momentum  $J$  for the vibrational transition  $00^00 \rightarrow 01^00$  of the  $\text{CO}_2$  molecule and for  $P$ ,  $Q$  and  $R$ -branches [10]



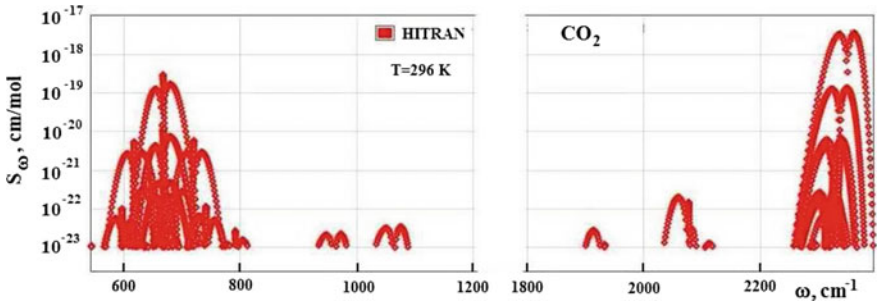
Considering the absorption coefficient due to  $\text{CO}_2$  molecules as a result of vibrational-rotational transitions, we assume their parameters to be independent on the rotational excitation because of the large vibrational energy compared with the rotational one. Of course, this assumption restricts the accuracy of calculations. In order to estimate this accuracy, we analyze the dependence of parameters of radiative transitions between two vibrational states on the rotational momentum  $J$  using the data of the HITRAN bank [11], restricting by the strongest transition between the ground  $00^00$  and the lowest excited  $01^00$  vibrational states. As for the width  $\nu$  of the spectral line of this transition due to collisions with air molecules at atmospheric pressure, this value is practically identical for the branches  $P$ ,  $Q$  and  $R$ , but depend on the rotational number  $J$ . This dependence is given in Fig. 4.6.

Figure 4.7 contains the dependence of the first Einstein coefficient  $A(\omega)$  on the rotational momentum  $J$  for the vibrational transition  $00^00 \rightarrow 01^00$  of the  $\text{CO}_2$  molecule in the cases of  $P$ ,  $Q$  and  $R$ -branches. We consider above two cases of momentum coupling which lead to relations (4.1.17) and (4.1.19); these relations correspond to different ratios of the energy difference for neighboring rotational levels to the interaction potential between deformation oscillation and rotation. One can expect that the first case of momentum coupling holds true that leads to formulas (4.1.17) for the probability of various transition branches. Nevertheless, real values of probabilities for various branches of radiative transitions according to Fig. 4.7 data relate to the second case of momentum coupling.

The absorption coefficient due to  $\text{CO}_2$  molecules is the sum of absorption coefficients for  $P$ ,  $Q$  and  $R$  branches which describe the absorption process in different spectrum ranges. One can see that  $Q$ -branch is included in the total absorption coefficient which has the form of a narrow peak, while  $P$  and  $R$ -branches give oscillating functions in a more wide range. We now use the above formulas for the absorption coefficient for atmospheric carbon dioxide in atmospheres of the Earth and Venus. Taking the average temperature of the Earth's surface to be  $T = 288$  K, we obtain that four vibrational transitions create emission of the atmosphere due to  $\text{CO}_2$  molecules,



**Fig. 4.8** Total absorption coefficient  $k_\omega$  at the Earth’s surface due to atmospheric carbon dioxide molecules for the standard atmosphere model according to formula (4.2.33) [31]

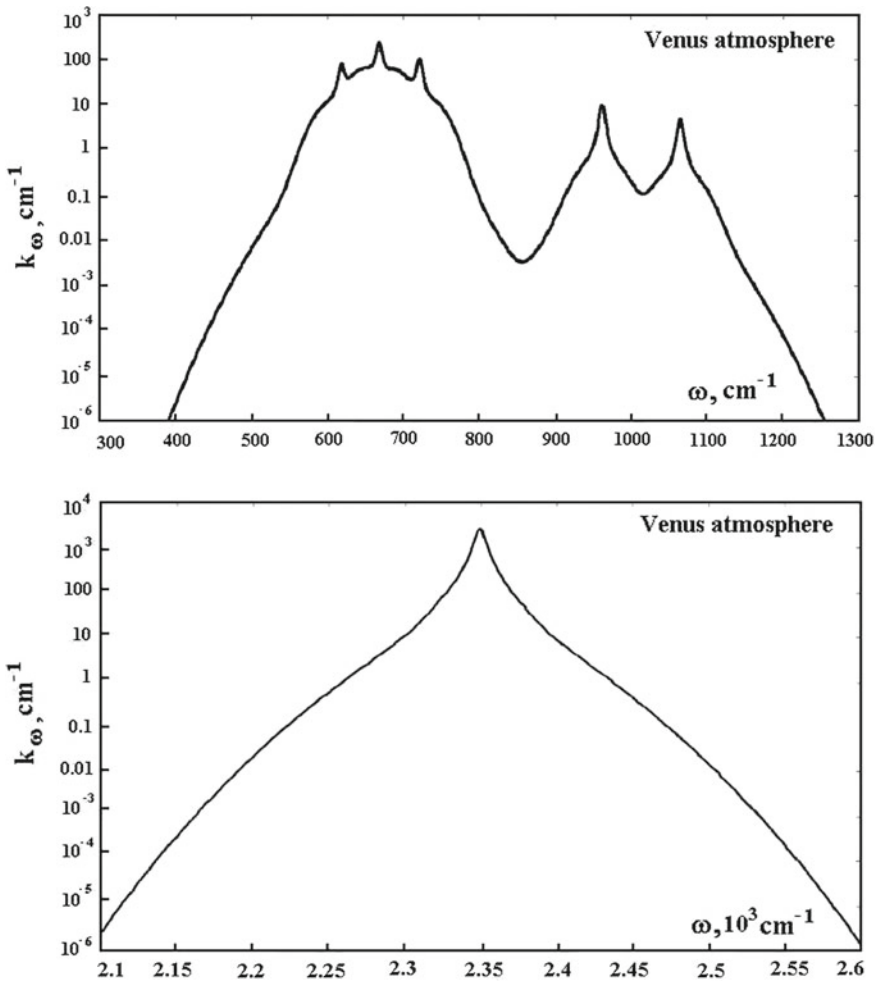


**Fig. 4.9** Intensity of spectral lines due to absorption by carbon dioxide molecules in atmospheric air according to data of HITRAN bank [10]

so that the absorption coefficient due to  $\text{CO}_2$  molecules as a frequency function has the form

$$k_\omega = \sum_{i=1}^4 k_\omega = \chi_{(\omega)}^{(i)} \varphi^{(i)}(\omega) + q_{(\omega)}^{(i)}, \quad (4.2.33)$$

Here components of this expression are given by formulas (4.2.18), (4.2.21), (4.2.28), and subindex indicates the number of the vibrational transition with accounting for lower transitions of Fig. 4.3. Figure 4.8 represents the atmospheric absorption coefficient due to  $\text{CO}_2$  molecules near the Earth surface for frequencies which determine the radiative flux to the Earth which is emitted by the atmosphere due to  $\text{CO}_2$  molecules. We take into account an atmospheric pressure near the Earth’s surface; the concen-



**Fig. 4.10** The absorption coefficient  $k_{\omega}$  near the surface of Venus due to carbon dioxide molecules, calculated on the basis of formula (4.2.31) [32]

tration  $c = 0.04\%$  for  $\text{CO}_2$  molecules that corresponds to their number density near the Earth surface  $N_v = 1 \cdot 10^{16} \text{ cm}^{-3}$ .

As it follows from Fig. 4.8, three radiative vibrational transitions determine the absorption coefficient in the  $\text{CO}_2$  molecule at the room temperature. This means that the radiative flux in the infrared spectrum range is determined by these three vibrational transitions which screen more weak vibrational transitions. The same conclusion follows from the analysis of the HITRAN bank data for the spectral line intensity which is presented in Fig. 4.9.

In the same manner, one can determine the absorption coefficient due to carbon dioxide molecules in the Venus atmosphere. The temperature of the Venus surface is



737 K, the pressure is 92 atm and the main part of the atmospheric gas is the carbon dioxide. This pressure leads to a large width of spectral lines, and neighboring lines are overlapped, so that  $\varphi^{(i)}(\omega) = 1$ . In addition, because of a high temperature, there are six vibrational-rotational transitions presented in Fig. 4.3. Therefore, the absorption coefficient is given by the following formula

$$k_{\omega} = \sum_{i=1}^6 k_{\omega} = \chi_{(\omega)}^{(i)} + q_{(\omega)}^{(i)}, \quad (4.2.34)$$

Figure 4.10 gives the frequency dependence of the absorption coefficient due to the atmospheric carbon dioxide near the Venus surface.

## References

1. A.A. Radzig, B.M. Smirnov, *Reference Data on Atoms, Molecules and Ions* (Springer, Berlin, 1985)
2. G. Hancock, I.W.M. Smith, *Appl. Opt.* **10**, 1827 (1971)
3. A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton, Princeton University Press, 1957)
4. L.D. Landau, E.M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Oxford, 1965)
5. E.U. Condon, G.H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970)
6. <https://en.wikipedia.org/wiki/Table-of-Clebsh-Gordan-coefficients>
7. M. Born, J.R. Oppenheimer, *Annalen der Physik* **389**, 457 (1927)
8. A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1960)
9. <https://en.wikipedia.org/wiki/Infrared-spectroscopy>
10. <http://www.hitran.iao.ru/home>
11. <http://www.hitran.org/links/>
12. G. Herzberg, *Molecular Spectra and Molecular Structure* (Princeton, Van Nostrand Reinhold, 1945)
13. M.A. El'yashevich, *Molecular Spectroscopy* (Moscow, Fizmatgiz, 1963; in Russian)
14. H.C. Allen, P.C. Cross, *Molecular Vib-Rotors; the Theory and Interpretation of High Resolution Infra-Red Spectra* (Wiley, New York, 1963)
15. G. Herzberg, *Molecular Spectra and Molecular Structure: Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966)
16. C.N. Banwell, E.M. McCash, *Fundamentals of Molecular Spectroscopy* (McGraw-Hill, London, 1994)
17. L.D. Kaplan, D.F. Eggers, *J. Chem. Phys.* **25**, 876 (1956)
18. J.E. Lowder, *JQSRT* **11**, 1647 (1971)
19. P. Varanasi, *JQSRT* **11**, 1711 (1971)
20. A. Levy, E. Piolet-Mariel, C. Boilet, *JQSRT* **13**, 673 (1973)
21. J.E. Lennard-Jones, A.E. Ingham, *Proc. Roy. Soc.* **106A**, 636 (1924)
22. J.E. Lennard-Jones, *Proc. Roy. Soc.* **107A**, 463 (1925)
23. B.M. Smirnov, *Phys. Uspekhi* **44**, 1229 (2001)
24. B.M. Smirnov, *Principles of Statistical Physics* (Wiley, Weinheim, 2006)
25. <http://www.hitran.org/docs/definitions-and-units/>
26. W.M. Elsasser, *Phys. Rev.* **54**, 126 (1938)
27. E.T. Whittaker, G.N. Watson, *Modern Analysis* (Cambridge University Press, London, 1940)

28. M.L. Salby, *Physics of the Atmosphere and Climate* (Cambridge University Press, Cambridge, 2012)
29. B.M. Smirnov, G.V. Schlyapnikov, *Sov. Phys. Uspekhi* **130**, 377 (1980)
30. B.M. Smirnov, *Plasma Processes and Plasma Kinetics* (Wiley, Weinheim, 2007)
31. B.M. Smirnov, *JETP* **126**, 446 (2018)
32. B.M. Smirnov, *JETP* **127**, 48 (2018)