9.5 Rotation and Vibration of Diatomic Molecules

Up to now we have discussed the electronic states of rigid molecules, where the nuclei are clamped to a fixed position. In this section we will improve our model of molecules and include the rotation and vibration of diatomic molecules. This means, that we have to take into account the kinetic energy of the nuclei in the Schrödinger equation $\hat{H}\psi = E\psi$, which has been omitted in the foregoing sections. We then obtain the Hamiltonian

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2}\sum_{k=1}^{2}\frac{1}{M_\mathrm{k}}\nabla_\mathrm{k}^2 - \frac{\hbar^2}{2m_\mathrm{e}}\sum_{i=1}^{N}\nabla_i^2 \\ &+\frac{e^2}{4\pi\varepsilon_0}\left[\frac{Z_1 Z_2}{R} + \sum_{i,j}\frac{1}{r_{i,j}} - \sum_i\left(\frac{1}{r_{i1}}+\frac{1}{r_{i2}}\right)\right] \\ &= \hat{E}_\mathrm{kin}^\mathrm{nucl} + E_\mathrm{kin}^\mathrm{el} + E_\mathrm{pot}^0 = \hat{T}_\mathrm{k} + \hat{H}_0 \qquad (9.73)\end{aligned}$$

where the first term represents the kinetic energy of the nuclei, the second term that of the electrons, the third represents the potential energy of nuclear repulsion, the fourth that of the electron repulsion and the last term the attraction between the electrons and the nuclei.

9.5.1 The Adiabatic Approximation

Because of their much larger mass, the nuclei in a molecule move much slower than electrons. This implies that the electrons can nearly immediately adjust their positions to the new nuclear configuration when the nuclei move. Although the electronic wave functions $\psi(r, R)$ depend parametrically on the internuclear distance R they are barely affected by the velocity of the moving nuclei. The kinetic energy of the nuclear motion $E_\mathrm{kin} = \frac{1}{2}Mv^2$ is small compared to that of the electrons. We therefore write the total Hamiltonian H in (9.73) as the sum

$$H = H_0 + T_\mathrm{k}$$

of the Hamiltonian H_0 of the rigid molecule and T_k of the kinetic energy of the nuclei. Since the latter is small compared to the total energy of rigid molecule we can regard T_k as a small perturbation of H. In this case the total wave function

$$\psi(\boldsymbol{r}_i, \boldsymbol{R}_\mathrm{k}) = \chi(\boldsymbol{R}_\mathrm{k})\cdot\Phi(\boldsymbol{r}_i, \boldsymbol{R}_\mathrm{k}) \qquad (9.74)$$

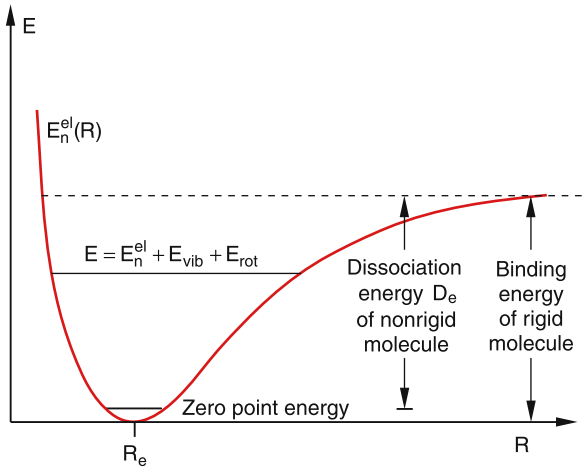


Fig. 9.41. Energy $E_n^\mathrm{el}(R)$ of the rigid molecule and total energy E of the nonrigid vibrating and rotating molecule

can be written as the product of the molecular wave function $\chi(\boldsymbol{R}_\mathrm{k})$ (which depends on the positions $\boldsymbol{R}_\mathrm{k}$ of the nuclei), and the electronic wave function $\Phi(\boldsymbol{r}_i, \boldsymbol{R}_\mathrm{k})$ of the rigid molecule at arbitrary but fixed nuclear positions $\boldsymbol{R}_\mathrm{k}$, where the electron coordinates $\boldsymbol{r}_i$ are the variables and $\boldsymbol{R}_\mathrm{k}$ can be regarded as a fixed parameter. This implies that nuclear motion and electronic motion are independent and the coupling between both is neglected. The total energy E is the sum of the energy $E_n^\mathrm{el}(R)$ of the rigid molecule in the nth electronic state, which is represented by the potential curve in Fig. 9.41 and the kinetic energy $(E_\mathrm{vib} + E_\mathrm{rot})$ of the nuclei.

Note that the total energy is independent of R!

Inserting this product into the Schrödinger equation (9.73) gives the two equations (see Problem 9.4)

$$\hat{H}_0\Phi_n^\mathrm{el}(\boldsymbol{r}, \boldsymbol{R}_\mathrm{k}) = E_n^{(0)}\cdot\Phi_n^\mathrm{el}(\boldsymbol{r}, \boldsymbol{R}_\mathrm{k}) \qquad (9.75a)$$

$$\left(\hat{T}_\mathrm{k} + E_n^{(0)}\right)\chi_{n,m}(\boldsymbol{R}) = E_{n,m}\chi_{n,m}(\boldsymbol{R})\,. \qquad (9.75b)$$

The first equation describes the electronic wave function Φ of the rigid molecule in the electronic state (n, L, Λ) and $E_n^{(0)}$ is the total electronic energy of this state without the kinetic energy T_k of the nuclei.

The second equation determines the motion of the nuclei in the potential

$$E_n^{(o)} = \left\langle E_\mathrm{kin}^\mathrm{el}\right\rangle + E_\mathrm{pot}(\boldsymbol{r}_i, \boldsymbol{R}_\mathrm{k})\,, \qquad (9.76)$$

which consists of the time average of the kinetic energy of the electrons and the total potential energy of electrons and nuclei. The total energy

$$E_{n,\mathrm{k}} = E_{\mathrm{kin}}^{\mathrm{nuc}} + E_n^{(o)} \tag{9.77}$$

of the nonrigid molecule is the sum of the kinetic energy of the nuclei and the total energy of the rigid molecule. Equation (9.75b) is explicitly written as

$$\left[\left(\frac{-\hbar^2}{2M_\mathrm{A}}\Delta_\mathrm{A} - \frac{-\hbar^2}{2M_\mathrm{B}}\Delta_\mathrm{B}\right) + E_{\mathrm{pot}}^{(n)}(\boldsymbol{R}_\mathrm{k})\right]\chi_{n,m}(\boldsymbol{R}_\mathrm{k}) = E_{n,m}\chi_{n,m}(\boldsymbol{R}_\mathrm{k})\,. \tag{9.78}$$

In the center of the mass system this translates to

$$\left[\frac{-\hbar^2}{2M}\Delta + E_{\mathrm{pot}}^{(n)}(R)\right]\chi_{n,m}(R) = E_{n,m}\chi_{n,m}(R) \tag{9.79}$$

where $M = M_\mathrm{A}M_\mathrm{B}/(M_\mathrm{A}+M_\mathrm{B})$ is the reduced mass of the two nuclei and the index m gives the mth quantum state of the nuclear movement (vibrational-rotational state).

The important result of this equation is:

> The potential energy for the nuclear motion in the electronic state (n, L, Λ) depends only on the nuclear distance R, not on the angles ϑ and φ, i. e., *it is independent of the orientation of the molecule in space*. It is spherically symmetric. The wave functions $\chi = \chi(R, \vartheta, \varphi)$, however, may still depend on all three variables R, ϑ, and φ.

Because of the spherically symmetric potential equation (9.77) is mathematically equivalent to the Schrödinger equation of the hydrogen atom. The difference lies only in the different radial dependence of the potential. Analogous to the treatment in Sect. 4.3.2 we can separate the wave functions $\chi(R, \vartheta, \varphi)$ into a radial part depending solely on R and an angular part, depending solely on the angles ϑ and φ. We therefore try the product ansatz

$$\chi(R, \vartheta, \varphi) = S(R)\cdot Y(\vartheta, \varphi)\,.$$

The radial function $S(R)$ depends on the radial form of the potential, while the spherical surface harmonics $Y(\vartheta, \varphi)$ are solutions for *all* spherically symmetric potentials, independent of their radial form.

Inserting the product (9.80) into (9.79) gives, as has been already shown in Sect. 4.3.2, the following equation for the radial function $S(R)$:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2M}{\hbar^2}\left[E - E_{\mathrm{pot}}(R) - \frac{J(J+1)\hbar^2}{2MR^2}\right]S = 0\,. \tag{9.80}$$

For the spherical surface harmonics $Y(\vartheta, \varphi)$ we obtain the Eq. (4.88), already treated in Sect. 4.4.2:

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2} + J(J+1)Y = 0\,. \tag{9.81}$$

While the first Eq. (9.80) describes the vibration of the diatomic molecule, (9.81) determines its rotation.

9.5.2 The Rigid Rotor

A diatomic molecule with the atomic masses M_A and M_B can rotate around any axis through the center of mass with the angular velocity ω (Fig. 9.42). Its rotational energy is then

$$E_{\mathrm{rot}} = \tfrac{1}{2}I\omega^2 = J^2/(2I)\,. \tag{9.82}$$

Here $I = M_\mathrm{A}R_\mathrm{A}^2 + M_\mathrm{B}R_\mathrm{B}^2 = MR^2$ where $M = M_\mathrm{A}M_\mathrm{B}/(M_\mathrm{A}+M_\mathrm{B})$ is the moment of inertia of the molecule with respect to the rotational axis and $|J| = I\omega$ is its rotational angular momentum. Since the square of the angular momentum

$$|J|^2 = J(J+1)h^2$$

can take only discrete values that are determined by the rotational quantum number J, the rotational energies of a molecule in its equilibrium position with an internuclear distance R_e are represented by a series of

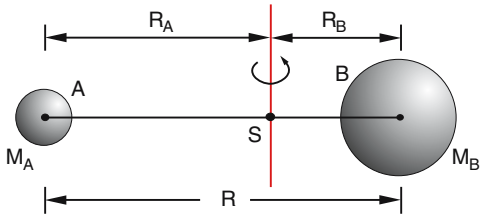


Fig. 9.42. Diatomic molecule as a rigid rotor

discrete values

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2MR_e^2} \quad . \tag{9.83}$$

The energy separation between the rotational levels J and $J+1$

$$\Delta E_{\text{rot}} = E_{\text{rot}}(J+1) - E_{\text{rot}}(J) = \frac{(J+1)\hbar^2}{2MR_e^2} \tag{9.84}$$

increases linearly with J (Fig. 9.43).

This result can also be directly obtained from (9.80). For a fixed nuclear distance R the first term in (9.80) is zero. Therefore the second term must also be zero, because the sum of the two terms is zero. The kinetic energy of a rigid rotor, which does not vibrate, is $E_{\text{kin}} = E_{\text{rot}} = E - E_{\text{pot}}$, where E is the total energy. The bracket of the second term in (9.80) then becomes for $R = R_e$ equal to (9.83).

In the spectroscopic literature, the rotational term values $F(J) = E(J)/hc$ are used instead of the energies. Instead of (9.83) we write

$$F_{\text{rot}}(J) = \frac{J(J+1)\hbar^2}{2hcMR_e^2} = B_e J(J+1) \tag{9.85}$$

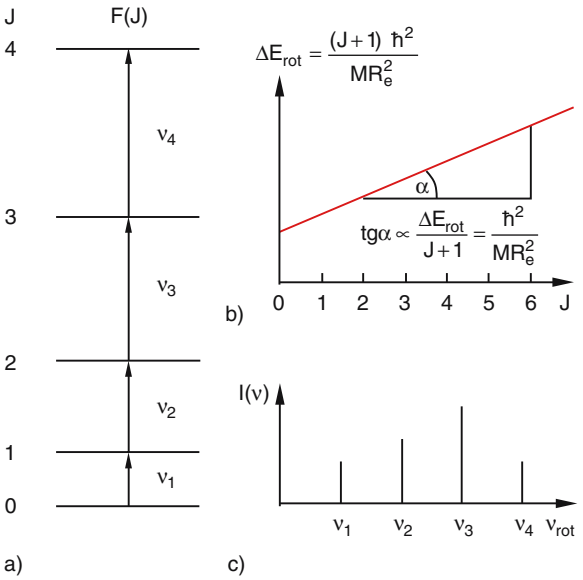


Fig. 9.43. (**a**) Energy levels of the rigid rotor (**b**) Separations $\Delta E_{\text{rot}} = E_{\text{rot}}(J+1) - E_{\text{rot}}(J)$ (**c**) Schematic rotational spectrum

with the rotational constant

$$B_e = \frac{\hbar}{4\pi c M R_e^2} \, , \tag{9.86}$$

which is determined by the reduced mass M and the equilibrium nuclear distance R_e. For historical reasons one writes B_e in units of cm^{-1} instead of m^{-1}.

EXAMPLES

1. The H_2 molecule has a reduced mass $M = 0.5 M_H = 8.35 \times 10^{-28}$ kg, and the equilibrium distance $R_e = 0.742 \times 10^{-10}$ m $\Rightarrow I = 4.60 \times 10^{-48}$ kg m^2. The rotational energies are

$$E_{\text{rot}}(J) = 1.2 \times 10^{-21} \, J(J+1) \text{ Joule}$$
$$= 7 J(J+1) \text{ meV} \, .$$

   The rotational constant is $B_e = 60.80\,\text{cm}^{-1}$.
2. For the HCl molecule the figures are $M = 0.97$ AMU $= 1.61 \times 10^{-27}$ kg, $R_e = 1.27 \times 10^{-10}$ m $\Rightarrow E_{\text{rot}} = 2.1 \times 10^{-22} \, J(J+1)$ Joule $= 1.21 \, J(J+1)$ meV, $B_e = 10.59\,\text{cm}^{-1}$.

In Table 9.7 the equilibrium distances R_e and the rotational constants are listed for some diatomic molecules. The figures show that the rotational energies are within the range of

$$E_{\text{rot}} = (10^{-6} - 10^{-2}) \, J(J+1) \text{ eV} \, .$$

For a rotational angular momentum J the rotational period becomes

$$T_{\text{rot}} = \frac{2\pi I/\hbar}{\sqrt{J(J+1)}} \, . \tag{9.87}$$

Depending on the rotational constant B_e they range from $T_{\text{rot}} = 10^{-14}$ s to 10^{-10} s. For $B_e = 1\,\text{cm}^{-1}$ one obtains $T_{\text{rot}} = 1.6 \times 10^{-11}/\sqrt{J(J+1)}$ s. If an electro-magnetic wave falls onto a sample of molecules it can be absorbed on rotational transitions $J \to J+1$ resulting in absorption lines with frequencies

$$\nu_{\text{rot}}(J) = [E(J+1)] - E(J)]/\hbar \tag{9.88a}$$

or, in wavenumber units cm^{-1},

$$\overline{\nu}_{\text{rot}}(J) = 2B_e(J+1) \, . \tag{9.88b}$$

The rotational transitions between levels J and $J+1$ fall into the spectral range with frequencies

Table 9.7. Equilibrium distances and rotational and vibrational constants in units of cm^{-1} for some diatomic molecules

Molecule	R_e/pm	B_e	D_e	α_e	ω_e	$\omega_e x_e$
H_2	74.16	60.8	1.6×10^{-2}	3.06	4401	121.3
Li_2	267.3	0.673	9.9×10^{-6}	0.007	351.4	2.6
N_2	109.4	2.01	5.8×10^{-6}	0.017	2359.0	14.3
O_2	120.7	1.45	4.8×10^{-6}	0.016	1580.0	12.0
I_2	266.6	0.037	4.2×10^{-9}	0.0001	214	0.61
$H^{35}Cl$	127.4	10.59	5.3×10^{-4}	0.31	2990	52.8
$D^{35}Cl$	127.4	5.45	1.4×10^{-4}	0.11	2145	27.2
ICl	232.1	0.114	4.0×10^{-8}	0.0005	384	1.50
CO	112.8	1.931	6×10^{-6}	0.017	2170	13.29
NO	115.1	1.705	0.5×10^{-6}	0.017	1904	14.08

$\nu = 10^9 - 10^{13}$ Hz, i.e., in the Gigahertz–Terrahertz range with wavelengths between $\lambda = 10^{-5} - 10^{-1}$ m. This spectral region is called the *microwave range*.

In Sect. 9.6.2 we will see, that only molecules with a permanent electric dipole moment can absorb or emit radiation on rotational transitions (except for very weak quadrupole transitions). Therefore homonuclear diatomic molecules show no rotational absorption or emission spectra!

9.5.3 Centrifugal Distortion

A real molecule is not rigid. When it rotates, the centrifugal force acts on the atoms and the internuclear distance widens to a value R where this force $F_c = -M\omega^2 R$ is compensated by the restoring force $F_r = -\mathrm{d}E_{pot}(R)/\mathrm{d}R$ holding the two atoms together, which depends on the slope of the potential energy function $E_{pot}(R)$ (Fig. 9.44).

In the vicinity of the equilibrium distance R_e the potential can be approximated by a parabolic function (see Sect. 9.4.4). This leads to a linear restoring force

$$\boldsymbol{F}_r = -k(R - R_e)\hat{R} \,. \tag{9.89}$$

From the relation $J^2 = I^2\omega^2 = M^2R^4\omega^2$ we obtain:

$$M\omega^2 R = \frac{J(J+1)\hbar^2}{MR^3} \stackrel{!}{=} k(R - R_e)$$
$$\Rightarrow R = R_e + \frac{J(J+1)\hbar^2}{MkR^3} \,, \tag{9.90}$$

which means that the internuclear distance R is widened by the molecular rotation. Since the potential energy $E_{pot}(R)$ is, for $R > R_e$, larger than $E_{pot}(R_e)$ we have to include the additional energy $\Delta E_{pot} = \frac{1}{2}k(R - R_e)^2$ in the rotational energy of the nonrigid rotor. The total energy of the nonrigid rotor is then

$$E_{rot} = \frac{J(J+1)\hbar^2}{2MR^2} + \frac{1}{2}k(R - R_e)^2 \,. \tag{9.91}$$

If we express R on the right side of (9.90) by R_e and k with the help of (9.89) we obtain

$$R = R_e\left(1 + \frac{J(J+1)\hbar^2}{MkR_e^4}\right) = R_e(1+x)$$

with $x \ll 1$. This allows us to expand $1/R^2$ into the power series

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left[1 - \frac{2J(J+1)\hbar^2}{MkR_e^4} + \frac{3J^2(J+1)^2\hbar^4}{M^2kR_e^8} \mp \dots\right] \tag{9.92}$$

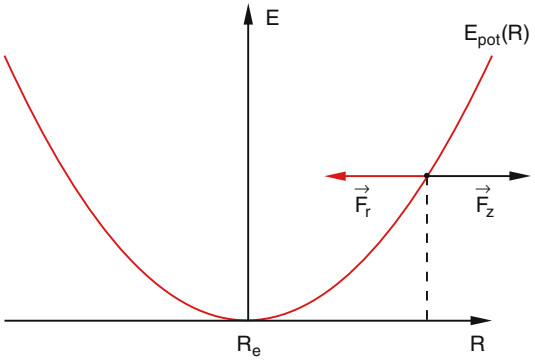


Fig. 9.44. Compensation of centrifugal and restoring force in the nonrigid rotating molecule

and the rotational energy becomes

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2MR_e^2} - \frac{J^2(J+1)^2\hbar^4}{2M^2kR_e^6} + \frac{3J^3(J+1)^3\hbar^6}{2M^3k^2R_e^{10}} \pm \dots . \tag{9.93}$$

For a given value of the rotational quantum number J the centrifugal widening makes the moment of inertia larger and therefore the rotational energy smaller. This effect overcompensates for the increase in potential energy.

Using the term-values instead of the energies, (9.94) becomes

$$F_{\text{rot}}(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 - \dots \tag{9.94}$$

with the rotational constants

$$B_e = \frac{\hbar}{4\pi cMR_e^2}, \quad D_e = \frac{\hbar^3}{4\pi ckM^2R_e^6}, \quad H_e = \frac{3\hbar^5}{4\pi ck^2M^3R_e^{10}} . \tag{9.95}$$

The spectroscopic accuracy is nowadays sufficiently high to measure even the higher order constant H. When fitting spectroscopic data by (9.95) this constant, therefore, has to be taken into account.

9.5.4 The Influence of the Electron Motion

Up to now we have neglected the influence of the electron motion on the rotation of molecules. In the axial symmetric electrostatic field of the two nuclei in the nonrotating molecule, the electrons precess around the space-fixed molecular z-axis. The angular momentum $\boldsymbol{L}(R) = \Sigma \boldsymbol{l}_i(R)$ of the electron shell, which depends on the separation R of the nuclei, has, however, a constant projection

$$\langle L_z \rangle = \Lambda h \tag{9.96a}$$

independent of R. For molecular states with electron spin $\boldsymbol{S} \neq 0$ in atoms with weak spin-orbit coupling the spin $\boldsymbol{S}$ precesses independently around the z-axis with a projection

$$\langle S_z \rangle = M_s h . \tag{9.96b}$$

Both projections add to the total value

$$\Omega h = (\Lambda + M_s)h . \tag{9.96c}$$

In the case of strong spin-orbit coupling $\boldsymbol{L}$ and $\boldsymbol{S}$ couple to $\boldsymbol{J}^{\text{el}} = \boldsymbol{L} + \boldsymbol{S}$ with the projection

$$\left\langle J_z^{\text{el}} \right\rangle = \Omega \times h$$

(see Sect. 9.3.3).

The total angular momentum J of the rotating molecule is now composed of the angular momentum $\boldsymbol{N}$ of the molecular rotation and the projection Λh or Ωh. For $\Omega \neq 0$ the total angular momentum $\boldsymbol{J}$ of the molecule is no longer perpendicular to the z-axis (Fig. 9.45).

Since the total angular momentum of a free molecule without external fields is constant in time, the molecule rotates around the space-fixed direction of J and for $\Lambda \neq 0$ the rotational axis is no longer perpendicular to the molecular z-axis.

In a simple model, the whole electron shell can be regarded as a rigid charge distribution that rotates around the z-axis. The rotating molecule can then be described as a symmetric top with two different moments of inertia: 1.) The moment I_1 of the electron shell rotating around the z-axis and 2.) the moment I_2 of the molecule

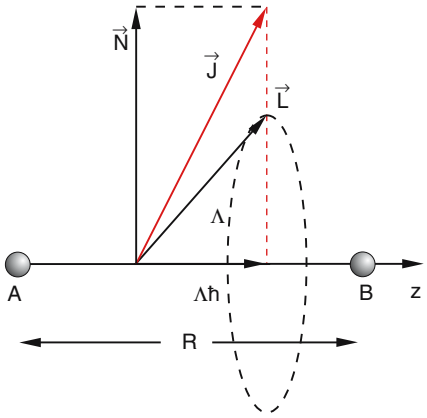


Fig. 9.45. Angular momenta of the rotating molecule including the electronic contribution

(nuclei and electrons) rotating around an axis perpendicular to the z-axis. Because the electron masses are very small compared with the nuclear masses, it follows that $I_1 \ll I_2$.

The rotational energy of this symmetric top is

$$E_{\text{rot}} = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \qquad (9.97)$$

$$\text{with} \quad I_x = I_y = I_1 \neq I_z = I_2 \,.$$

From Fig. 9.45 the following relations can be obtained:

$$\begin{aligned} J_z^2 &= \Omega^2\hbar^2 \\ \boldsymbol{J}_x^2 + \boldsymbol{J}_y^2 &= N^2\hbar^2 = J^2 - J_z^2 \\ &= \left[J(J+1) - \Omega^2\right]\hbar^2 \,. \end{aligned} \qquad (9.98)$$

Inserting this into (9.97) gives the term values $F(J) = E_{\text{rot}}(J)/hc$ of the rotational levels

$$\boxed{F(J,\Omega) = B_{\text{e}}\left[J(J+1) - \Omega^2\right] + A\Omega^2} \qquad (9.99)$$

with the two rotational constants

$$A = \frac{\hbar}{4\pi c I_1} \gg B_{\text{e}} = \frac{\hbar}{4\pi c I_2} \,. \qquad (9.100)$$

The term $A\Omega^2$, which does not depend on J, is generally added to the electronic energy T_{e} of the molecular state, since it is constant for all rotational levels of a given electronic state with quantum number Ω. It is therefore also not influenced by the centrifugal distortion.

The ground states of the majority of diatomic molecules are $^1\Sigma$-states with $\Lambda = \Omega = 0$. For these cases $A = 0$ and (9.99) is identical to (9.94).

9.5.5 Vibrations of Diatomic Molecules

For a nonrotating molecule, the rotational quantum number J in (9.80) is zero. The solutions $S(R)$ of (9.80) are then the vibrational wave functions of the diatomic molecule. For $J = 0$ they solely depend on the radial form of the potential energy $E_{\text{pot}}(R)$. For a parabolic potential, the vibrating molecule is a harmonic oscillator, which has been already treated in Sect. 4.2.5. The result obtained there was the quantization of the energy levels.

The energy levels of the harmonic oscillator

$$E(v) = (v + \tfrac{1}{2})h\omega \qquad (9.101)$$

depend on the integer vibrational quantum number $v = 0, 1, 2, \ldots$.

They are equally spaced by $\Delta E = \hbar\omega$. The frequency $\omega = \sqrt{k_{\text{r}}/M}$ depends on the constant $k_{\text{r}} = (\mathrm{d}^2 E_{\text{pot}}/\mathrm{d}R^2)_{R_{\text{e}}}$ in the parabolic potential and on the reduced mass M of the molecule. The lowest vibrational level is not $E = 0$ but $E = \frac{1}{2}\hbar\omega$. The solutions of (9.80) with a parabolic potential are the vibrational eigenfunctions

$$S(R) = \psi_{\text{vib}}(R, v) = e^{-\pi M\omega/hR} \cdot H_{\text{v}}(R) \qquad (9.102)$$

where the functions $H_{\text{v}}(R)$ are the Hermitian polynomials. Some of these vibrational eigenfunctions of the harmonic oscillator are compiled in Table 4.1 and are illustrated in Fig. 4.20.

Although the real potential of a diatomic molecule can be well approximated by a parabolic potential in the vicinity of the potential minimum at $R = R_{\text{e}}$, it deviates more and more for larger $|R - R_{\text{e}}|$ (see Fig. 9.38). This figure also illustrates that the Morse potential is a much better approximation. Inserting the Morse potential

$$E_{\text{pot}}(R) = E_{\text{D}}\left[1 - e^{-a(R-R_{\text{e}})}\right]^2 \qquad (9.103)$$

into the radial part (9.80) of the Schrödinger equation allows its exact analytical solution (see Problem 9.5). The energy eigenvalues are now:

$$E_{\text{vib}}(v) = \hbar\omega_0\left(v + \frac{1}{2}\right) - \frac{\hbar^2\omega_0^2}{4E_{\text{D}}}\left(v + \frac{1}{2}\right)^2 \qquad (9.104)$$

with energy separations

$$\begin{aligned} \Delta E(v) &= E_{\text{vib}}(v+1) - E_{\text{vib}}(v) \qquad (9.105\text{a}) \\ &= \hbar\omega\left[1 - \frac{\hbar\omega}{2E_{\text{D}}}(v+1)\right] \,, \end{aligned}$$

where E_{D} is the dissociation energy of the rigid molecule. The vibrational levels are no longer equidistant but separations decrease with increasing vibrational quantum number v, in accordance with experimental observations.

The term-values $T_v = E_v/hc$ are

$$T_{\text{vib}}(v) = \omega_{\text{e}}(v + \tfrac{1}{2}) - \omega_{\text{e}}x_{\text{e}}(v + \tfrac{1}{2}) \qquad (9.105\text{b})$$

with the vibrational constants

$$\omega_{\text{e}} = \frac{\omega_0}{2\pi c} \,, \quad \omega_{\text{e}}x_{\text{e}} = \frac{\hbar\omega_0^2}{8\pi c E_{\text{D}}} = \omega_{\text{e}}^2\frac{hc}{4E_{\text{D}}} \,. \qquad (9.105\text{c})$$

The vibrational frequency

$$\omega_0 = a\sqrt{2E_D/M} \tag{9.106}$$

corresponds to that of a classical oscillator with the restoring force constant $k_r = 2a^2 E_D$. From measurements of k_r (for instance from the centrifugal distortion of rotational levels) and the dissociation energy E_D the constant a in the Morse potential can be determined.

With the more general expansion of the potential

$$E_{pot}(R) = \sum_n \frac{1}{n!}\left(\frac{\partial^n E_{pot}}{\partial R^n}\right)_{R_e} (R - R_e)^n \tag{9.107}$$

the Schrödinger equation can only be solved numerically. We will, however, see in Sect. 9.5.7 that the real potential can be very accurately determined from the measured term values of the rotational and vibrational levels.

Note:

- The distance between vibrational levels decreases with increasing v, but stays finite up to the dissociation energy. This means that only a finite number of vibrational levels fit into the potential well of a bound molecular state. This is in contrast to the infinite number of electronic states in an atom such as the H atom. Here the distance between Rydberg levels converges with $n \to \infty$ towards zero (see (3.88)). This different behavior stems from the different radial dependence of the potentials in the two cases.
- One has to distinguish between the experimentally determined dissociation energy E_D^{exp}, where the molecule is dissociated from its lowest vibration level, and the binding energy E_B of the potential well, which is measured from the minimum of the potential (Fig. 9.41). The difference is

$$E_D^{exp} = E_B - \tfrac{1}{2}\hbar\omega\,.$$

9.5.6 Interaction Between Rotation and Vibration

Up to now we have looked at the rotation of a nonvibrating molecule and the vibration of a nonrotating molecule. Of course a real molecule can simultaneously rotate and vibrate. Since the vibrational frequency is higher than the rotational frequency by one to two orders of magnitude, the molecule undergoes many vibrations (typically 5–100) during one rotational period (Fig. 9.46). This means that the nuclear distance changes periodically during one full rotation.

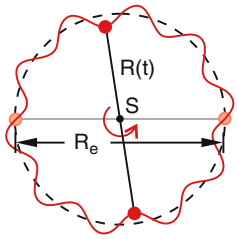


Fig. 9.46. Vibrating rotor

EXAMPLES

1. For the H_2 molecule, $\omega_e = 1.3\times10^{14}\,s^{-1} \Rightarrow T_{vib} = 4.8\times10^{-14}\,s$, while $T_{rot} = 2.7\times10^{-13}\sqrt{J(J+1)}\,s$.
2. For the Na molecule, $\omega_e = 4.5\times10^{12}\,s^{-1} \Rightarrow T_{vib} = 1.4\times10^{-12}\,s$, while $T_{rot} = 1.1\times10^{-10}\sqrt{J(J+1)}\,s$.

Since the total angular momentum $J = I\cdot\omega$ of a freely rotating molecule has to be constant in time, but the moment of inertia I periodically changes, the rotational frequency ω has to change accordingly with a period T_{vib}. Therefore the rotational energy

$$E_{rot} = \frac{J(J+1)\hbar^2}{2mR^2}$$

also varies periodically with a period T_{vib}.

Because the total energy $E = E_{rot} + E_{vib} + E_{pot}$ has to be constant, there is a periodic exchange of rotational, vibrational and potential energy in the vibrating rotor (Fig. 9.47).

The rotational energy, considered separately, is the time average over a vibrational period. This time average can be calculated as follows:

The probability to find the nuclei within the interval dR around the distance R is

$$P(R)\,dR = |\psi_{vib}(R)|^2\,dR\,.$$

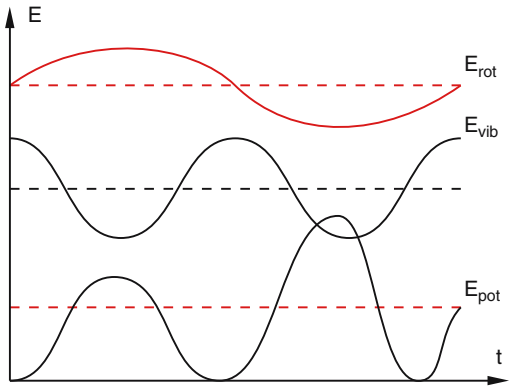


Fig. 9.47. Exchange between rotational, vibrational and potential energy during a vibrational period

The quantum mechanical expectation values of R and $1/R^2$ are then

$$\langle R\rangle = \int \psi^*_{\text{vib}} R \psi_{\text{vib}}\,\mathrm{d}R\,, \textit{ and} \tag{9.108}$$
$$\langle 1/R^2\rangle = \int \psi^*_{\text{vib}} \frac{1}{R^2} \psi_{\text{vib}}\,\mathrm{d}R\,.$$

This gives the mean rotational energy, averaged over one vibrational period

$$\langle E_{\text{rot}}(v)\rangle = \frac{J(J+1)\hbar^2}{2M} \int \psi^*_{\text{vib}}(v) \frac{1}{R^2} \psi_{\text{vib}}(v)\;\mathrm{d}R\,. \tag{9.109}$$

Note:

Even for a harmonic potential the expectation value of $1/R^2$ depends on the vibrational quantum number v. It increases with v although $\langle R\rangle$ is independent of v and always equal to R_e (Fig. 9.48). Therefore, the rotational constant B_v of the rotating harmonic oscillator also depends on v. For the more realistic anharmonic potential, both $\langle R\rangle$ as well as $\langle 1/R^2\rangle$ change with v. While $\langle R\rangle$ increases $\langle 1/R^2\rangle$ decreases with increasing v.

In order to express the rotational term values by a rotational constant similar to (9.86) or (9.95) we introduce, instead of B_e, the rotational constant

$$B_v = \frac{\hbar}{4\pi c M} \int \psi^*_{\text{vib}}(v, R) \frac{1}{R^2} \psi_{\text{vib}}(v, R)\,\mathrm{d}R \tag{9.110a}$$

averaged over the vibrational motion. It depends on the vibrational quantum number v.

For a Morse potential we then obtain

$$B_v = B_\text{e} - \alpha_\text{e}(v+\tfrac{1}{2}) \tag{9.111a}$$

where $\alpha_\text{e} \ll B_\text{e}$. In a similar way an average centrifugal constant

$$D_v = \frac{\hbar^3}{4\pi c k M^2} \int \psi^*_{\text{vib}} \frac{1}{R^6} \psi_{\text{vib}}\,\mathrm{d}R \tag{9.110b}$$

can be defined, which is related to D_e by

$$D_v = D_\text{e} - \beta_\text{e}(v+\tfrac{1}{2}) \quad \text{with} \quad \beta_\text{e} \ll D_\text{e}\,. \tag{9.111b}$$

For a general potential, higher order constants have to be introduced and one writes

$$B_v = \beta_\text{e} - \alpha_\text{e}(v+\tfrac{1}{2}) + \gamma_\text{e}(v+\tfrac{1}{2})^2 + \ldots \tag{9.112a}$$
$$D_v = D_\text{e} + \beta_\text{e}(v+\tfrac{1}{2}) + \delta_\text{e}(v+\tfrac{1}{2})^2 + \ldots\,. \tag{9.112b}$$

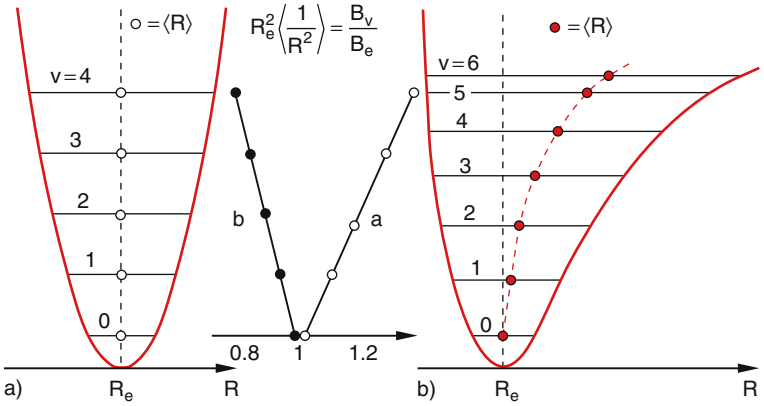


Fig. 9.48. Mean internuclear distance $\langle R\rangle$ and rotational constant $B_v \propto \langle 1/R^2\rangle$ for the harmonic (**a**)and anharmonic (**b**)potential

The term value of a rotational-vibrational level can then be expressed as the power series

$$\begin{aligned} T(v, J) = T_e + \big[&\omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 \\ &+ \omega_e y_e(v+\tfrac{1}{2})^3 + \omega_e z_e(v+\tfrac{1}{2})^4 + \dots\big] \\ &+ \big[B_v J(J+1) - D_v J^2(J+1)^2 \\ &+ H_v J^3(J+1)^3 \mp \dots\big] \,. \end{aligned} \tag{9.113a}$$

For a Morse potential this series is reduced to

$$\begin{aligned} T^{\text{Morse}}(v, J) = T_e &+ \omega_e(v+\tfrac{1}{2}) \\ &- \omega_e x_e(v+\tfrac{1}{2})^2 + B_v J(J+1) \\ &- D_v J^2(J+1)^2 \end{aligned} \tag{9.113b}$$

where only five constants describe the energies of all levels (v, J) up to energies where the Morse potential is still a good approximation.

9.5.7 The Dunham Expansion

In order to also reproduce the rotational-vibrational term values $T(v, J)$ of a rotating molecule for a more general potential (9.107)

$$E_{\text{pot}}(R) = \sum_n a_n (R - R_e)^n \,, \tag{9.114}$$

with

$$a_n = \frac{1}{n!}\left(\frac{\partial^n E_{\text{pot}}}{\partial R^n}\right)_{R_e} \,.$$

Dunham introduced the expansion

$$T(v, J) = \sum_i \sum_k Y_{ik}(v+\tfrac{1}{2})^i \left[J\cdot(J+1) - \Lambda^2\right]^k \tag{9.115}$$

where the Dunham coefficients Y_{ik} are fit parameters chosen such that the term values $T(v, J)$ best reproduce the measured term values of rotational levels in vibrational states of the molecule.

With (9.115) the energies of all vibrational-rotational levels of a molecule can be described by a set of molecular constants. These constants are related to the coefficients in the expansion (9.113a) by the relations

$$\begin{aligned} &Y_{10} \approx \omega_e \,, \quad Y_{20} \approx -\omega_e x_e \,, \quad Y_{30} \approx \omega_e y_e \\ &Y_{01} \approx B_e \,, \quad Y_{02} \approx D_e \,, \quad\quad Y_{03} \approx H_e \\ &Y_{11} \approx -\alpha_e \,, \quad Y_{12} \approx \beta_e \,, \quad\quad Y_{21} \approx \gamma_e \end{aligned} \tag{9.116}$$

and also to the coefficients a_n in the general potential expansion (9.114) [9.10].

9.5.8 Rotational Barrier

The effective potential for a rotating molecule (see (9.80))

$$E_{\text{pot}}^{\text{eff}}(R) = E_{\text{pot}}^{(v)}(R) + \frac{J(J+1)\hbar^2}{2MR^2} \tag{9.117}$$

includes, besides the potential $E_{\text{pot}}(R)$ of the nonrotating molecule, a centrifugal term that depends on the rotational quantum number J and falls of with R as $1/R^2$ (Fig. 9.49). For a bound electronic state this leads to a maximum of $E_{\text{pot}}^{\text{eff}}(R)$ at a distance R_m, which can be obtained by setting the first derivative of (9.117) to zero. This distance

$$R_m = \left[\frac{J(J+1)\hbar^2}{M(\mathrm{d}E_{\text{pot}}/\mathrm{d}R)}\right]^{1/3} \tag{9.118}$$

depends on the rotational quantum number J and on the slope of the rotationless potential.

The minimum of the potential is shifted by the rotation of the molecule from R_e to larger distances and the dissociation energy becomes smaller.

Energy levels $E(v, J)$ above the dissociation energy E_D can be still stable, if they are below the maximum of

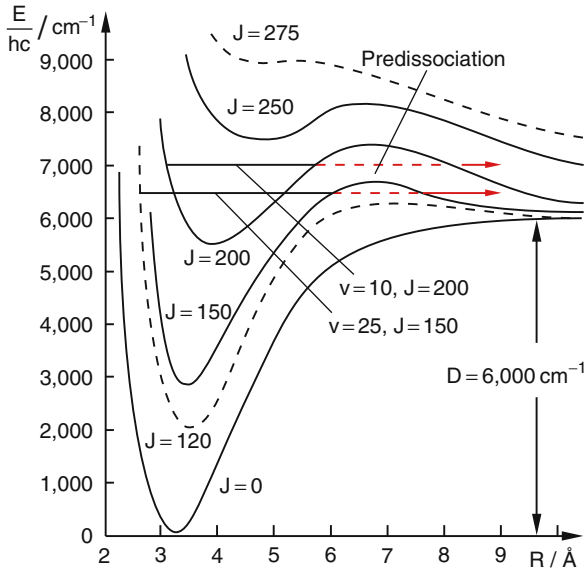


Fig. 9.49. Effective potential curves of the rotating Na_2 molecule for different rotational quantum number J

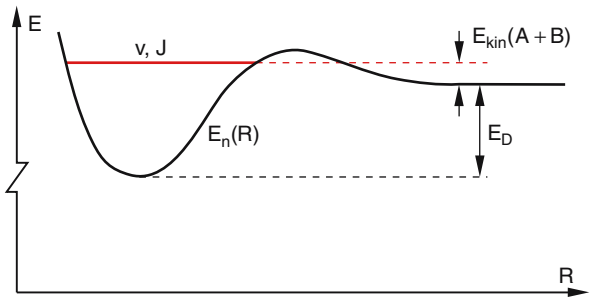


Fig. 9.50. Predissociation of a molecule through the rotational barrier

the potential barrier. However, due to the tunnel effect (Sect. 4.2.3) molecules in these levels can dissociate by tunneling through the barrier (Fig. 9.50). This effect is called predissociation by tunneling. The tunnel probability depends exponentially on the width of the barrier and on the energy gap between the maximum of the barrier and the level energy.

The predissociation rate can be determined by measuring the width $\delta E = h/\tau$ of levels with a lifetime τ. If the predissociation rate is large compared to the radiative decay of a level, the lifetime τ is mainly determined by predissociation. Measuring $\tau(v)$ for all levels above the dissociation limit gives information on the form and heights of the potential barrier.

The dissociating fragments have a kinetic energy

$$E_{\text{kin}} = E(v, J) - E_{\text{D}}(J = 0) ,$$

which is shared by the two fragments according to their masses.

9.6 Spectra of Diatomic Molecules

When a molecule undergoes a transition

$$E_i(n_i, \Lambda_i, v_i, J_i) \leftrightarrow E_k(n_k, \Lambda_k, v_k, J_k)$$

between two molecular states $|i\rangle$ and $|k\rangle$, electromagnetic radiation can be absorbed or emitted with a frequency $\nu = \Delta E/h$. Whether this transition really occurs depends on its transition probability, which is proportional to the absolute square of the dipole matrix element M_{ik} (see Sect. 7.1). The relative intensities of spectral lines can therefore be determined if the matrix elements of the transitions can be calculated. Because of the larger variety of molecular states, with energies depending on the electronic, the rotational and vibrational structure of the molecule, the matrix elements of molecules are more complicated than those of atoms. In this section we will discuss their structure and the molecular spectra derived from them.

For spontaneous emission (fluorescence spectra) the emission probability of a transition $|i\rangle \rightarrow |k\rangle$ is given by the Einstein coefficient A_{ik}. According to (7.17) A_{ik} is related to the transition dipole matrix element M_{iK} by

$$A_{ik} = \frac{2}{3}\frac{\omega_{ik}^3}{\varepsilon_0 c^3 \hbar} |\boldsymbol{M}_{ik}|^2 \ . \tag{9.119a}$$

For the absorption or stimulated emission of radiation the transition probability $P_{ik} = B_{ik} w(\nu_{ik})$ is proportional to the spectral energy density $w(\nu)$ of the radiation field. In Sect. 7.2 it was shown that P_{ik} is given by

$$P_{ik} = \frac{\pi}{2\hbar^2} E_0^2 \left| \psi_k^* \boldsymbol{\varepsilon} \cdot \boldsymbol{p} \psi_i \, \mathrm{d}\tau \right|^2 \tag{9.119b}$$

where $\boldsymbol{\varepsilon} = \boldsymbol{E}/|\boldsymbol{E}|$ is the unit vector in the direction of the electric field E of the electromagnetic wave, incident onto the molecules. The transition probability therefore depends on the scalar product $\boldsymbol{\varepsilon} \cdot \boldsymbol{p}$ of electric field vector and electric transition dipole of the molecule.

9.6.1 Transition Matrix Elements

The dipole matrix element for a transition between two molecular states with wave functions ψ_i and ψ_k is

$$\boldsymbol{M}_{ik} = \iint \psi_i^* \boldsymbol{p} \psi_k \, \mathrm{d}\tau_{\text{el}} \, \mathrm{d}\tau_{\text{N}} \ . \tag{9.119c}$$

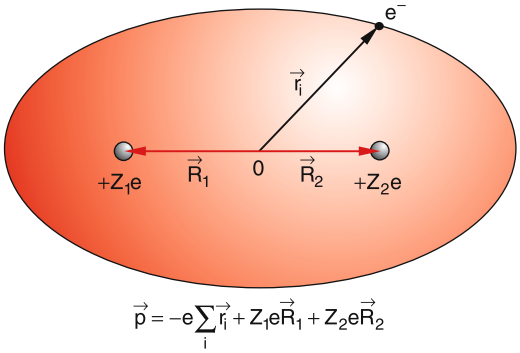


Fig. 9.51. Illustration of nuclear and electronic contributions to the molecular dipole moment

The integration extends over all $3(Z_A + Z_B)$ electronic coordinates and over the six nuclear coordinates. Often only one of the electrons is involved in the transition. In this case the integration over $d\tau_{el}$ only needs to be performed over the coordinates of this electron. The vector $\boldsymbol{p}$ is the dipole operator, which depends on the coordinates of the electrons, involved in the transition and on the nuclear coordinates. In Fig. 9.51 it can be seen that

$$\boldsymbol{p} = -e\sum_i \boldsymbol{r}_i + e(Z_A\boldsymbol{R}_A + Z_B\boldsymbol{R}_B) = \boldsymbol{p}_{el} + \boldsymbol{p}_N \tag{9.120}$$

where $\boldsymbol{p}_{el}$ is the contribution of the electrons and $\boldsymbol{p}_N$ that of the nuclei.

Note that for homonuclear molecules $Z_A = Z_B$ but $\boldsymbol{R}_A = -\boldsymbol{R}_B$. Therefore $\boldsymbol{p}_N = 0$!

Within the adiabatic approximation we can separate the total wave function $\psi(r, R)$ into the product

$$\psi(\boldsymbol{r}, \boldsymbol{R}) = \Phi(\boldsymbol{r}, \boldsymbol{R}) \times \chi_N(\boldsymbol{R}) \tag{9.121}$$

of electronic wave function $\Phi(r, R)$ of the rigid molecule at a fixed nuclear distance R and the nuclear wave function $\chi(R)$; which only depends on the nuclear coordinates. Inserting (9.120, 9.121) into (9.119) the matrix elements is written as

$$\boldsymbol{M}_{ik} = \iint \Phi_i^*\, \chi_{N,i}^*(\boldsymbol{p}_{el} + \boldsymbol{p}_N)\Phi_k\chi_{N,k}^*\, d\tau_{el}\, d\tau_N\,. \tag{9.122a}$$

Rearranging the different terms gives

$$\boldsymbol{M}_{ik} = \int \chi_i^* \left[\int \Phi_i^* \boldsymbol{p}_{el}\Phi_k\, d\tau_{el}\right]\chi_k\, d\tau_N + \int \chi_1^*\boldsymbol{p}_N\left[\int \Phi_i^*\Phi_k\, d\tau_{el}\right]\chi_k\, d\tau_N\,. \tag{9.122b}$$

We distinguish between two different cases (Fig. 9.52):

- The two levels $|i\rangle$ and $|k\rangle$ belong to the same electronic state ($\Phi_i = \Phi_k$). This means that the dipole transition occurs between two vibrational-rotational levels in the same electronic state Φ_i. In this case the first term in the sum (9.122b) is zero because the integrand $\boldsymbol{r}|\Phi_i|^2$ is an ungerade function of the electron coordinates $\boldsymbol{r} = \{x, y, z\}$. The integration from $-\infty$ to $+\infty$ therefore gives zero.

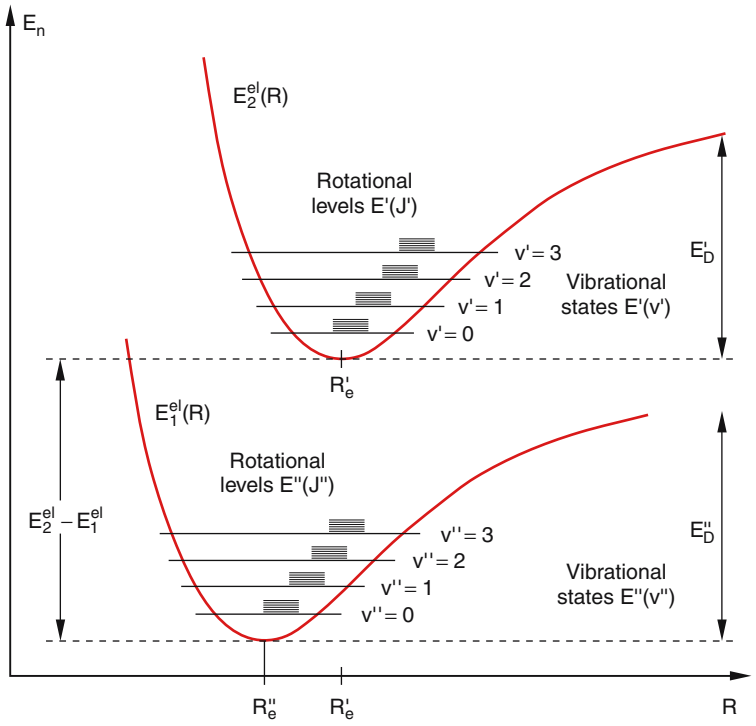


Fig. 9.52. Rotational and vibrational levels in two different electronic states of a diatomic molecule

Since the electronic wave functions Φ are orthonormal, i. e.,

$$\int \Phi_i^* \phi_k \, \mathrm{d}\tau_{\mathrm{el}} = \delta_{ik} \tag{9.123}$$

the integral over the electronic coordinates in the second term in the sum (9.122b) is equal to one. The matrix element then becomes

$$\boxed{\boldsymbol{M}_{ik} = \int \chi_{i,\mathrm{N}} \boldsymbol{p}_{\mathrm{N}} \chi_{k,\mathrm{N}} \, \mathrm{d}\tau_{\mathrm{N}}} \quad . \tag{9.124}$$

The integrand solely depends on the nuclear coordinates, not on the electronic coordinates!

- Transitions between levels in two different electronic states. In this case the integral over the electronic coordinates in the second term of (9.122b) is zero because the Φ_i, Φ_k are orthonormal. The second term is therefore zero and the matrix element becomes

$$\begin{aligned} \boldsymbol{M}_{ik} &= \int \chi_i^* \left[\int \Phi_i^* \boldsymbol{p}_{\mathrm{el}} \Phi_k \, \mathrm{d}\tau_{\mathrm{el}} \right] \chi_k \, \mathrm{d}\tau_{\mathrm{N}} \\ &= \chi_i^* \boldsymbol{M}_{ik}^{\mathrm{el}}(R) \chi_k \, \mathrm{d}\tau_{\mathrm{N}} \, . \end{aligned} \tag{9.125}$$

We will now discuss both cases separately.

9.6.2 Vibrational-Rotational Transitions

All allowed transitions $(v_i, J_i) \leftrightarrow (v_k, J_k)$ between two rotational-vibrational levels in the same electronic state form for $v_i \neq v_k$ the vibrational-rotational spectrum of the molecule in the infrared spectral region between $\lambda = 2 - 20\,\mu\mathrm{m}$. For $v_i = v_k$ we have pure rotational transitions between rotational levels within the same vibrational state, which form the rotational spectrum in the microwave region with wavelengths in the range $0.1 - 10\mathrm{cm}$.

The dipole matrix element for these transitions is according to (9.120) and (9.124)

$$\boldsymbol{M}_{ik}^{\text{rot vib}} = e \int \chi_i^* (Z_{\mathrm{A}} \boldsymbol{R}_{\mathrm{A}} + Z_{\mathrm{B}} \boldsymbol{R}_{\mathrm{B}}) \chi_k \, \mathrm{d}\tau_{\mathrm{N}} \, . \tag{9.126}$$

For homonuclear diatomic molecules with $Z_{\mathrm{A}} = Z_{\mathrm{B}}$ and $M_{\mathrm{A}} = M_{\mathrm{B}}$ is $R_{\mathrm{A}} = -R_{\mathrm{B}}$ and therefore the integrand is zero $\Rightarrow \boldsymbol{M}_{ik}^{\text{rot vib}} = 0$.

Homonuclear diatomic molecules have no dipole-allowed vibrational-rotational spectra. This means they do not absorb or emit radiation on transitions within the same electronic state. They may have very weak quadrupole transitions.

Note:

The molecules N_2 and O_2, which represent the major constituents of our atmosphere, cannot absorb the infrared radiation emitted by the earth. Other molecules, such as CO_2, H_2O, NH_3 and CH_4 do have an electric dipole moment and absorb infrared radiation on their numerous vibrational-rotational transitions. Although they are present in our atmosphere only in small concentrations they can seriously perturb the delicate energy balance between absorbed incident sun radiation and the energy radiated back into space by the earth (greenhouse effect). If their concentration is increased by only small amounts this can increase the temperature of the atmosphere at the earth's surface (greenhouse effect).

The structure of the vibration-rotation-spectrum and the pure rotation spectrum can be determined as follows.

Since the interaction potential between the two atoms is spherically symmetric, we choose spherical coordinates for the description of the nuclear wave function $\chi_{\mathrm{N}}(R, \vartheta, \varphi)$.

If the interaction between rotation and vibration is sufficiently weak we can write χ_{N} as the product

$$\chi_{\mathrm{N}}(R, \vartheta, \varphi) = S(R) Y_J^M(\vartheta, \varphi) \tag{9.127}$$

of the vibrational wave function $S(R)$ in (9.102) and the rotational wave function $Y_J^M(\vartheta, \varphi)$ for a rotational level with angular momentum J and its projection $M \cdot \hbar$ onto the quantization axis, which is a preferential direction in the laboratory coordinate system. For absorbing transition the quantization axis is, for instance, the direction of the incident electromagnetic wave, or the direction of its E-vector.

With $R = |\boldsymbol{R}_{\mathrm{A}} - \boldsymbol{R}_{\mathrm{B}}|$ and $R_{\mathrm{A}}/R_{\mathrm{B}} = M_{\mathrm{B}}/M_{\mathrm{A}}$ (Figs. 9.42 and 9.51) and $\hat{p} = \boldsymbol{p}/|p|$ the dipole moment can be written as

$$\begin{aligned} \boldsymbol{p}_{\mathrm{N}} = \hat{p} \cdot |p_{\mathrm{N}}| &= e \frac{M_{\mathrm{B}} \cdot Z_{\mathrm{A}} - M_{\mathrm{A}} \cdot Z_{\mathrm{B}}}{M_{\mathrm{A}} + M_{\mathrm{B}}} \cdot R \cdot \hat{p} \\ &= C R \hat{p} \, . \end{aligned} \tag{9.128}$$

The volume element in spherical coordinates is

$$\mathrm{d}\tau_N = R^2\,\mathrm{d}R\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi\,.$$

This gives the matrix element

$$\boldsymbol{M}_{ik} = C\cdot\int_R S^*_{v_i}(R)S_{v_k}(R)R^3\,\mathrm{d}R \qquad (9.129)$$
$$\times\int_{\vartheta,\varphi} Y^{M_i}_{J_i}Y^{M_k}_{J_k}\hat{\boldsymbol{p}}\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi\,.$$

The first factor describes the vibrational transition $v_i \leftrightarrow v_k$. If the harmonic oscillator functions are used for the vibrational functions $S(R)$ the calculations of the integral shows that the integral is zero, unless

$$\Delta v = v_i - v_k = 0 \quad \text{or} \quad \pm 1\,. \qquad (9.130)$$

The + sign stands for absorbing, the minus sign for emitting transitions. Transitions with $\Delta v = 0$ are pure rotational transitions within the same vibrational level.

This selection rule means that for the harmonic oscillator only transitions between neighboring vibrational levels are allowed.

For anharmonic potentials, such as the Morse potential, higher order transitions with $\Delta v = \pm 2, \pm 3, \ldots$ are also observed. Such *overtone-transitions* are, however, much weaker than the *fundamental transitions* with $\Delta v = \pm 1$.

The second integral in (9.129) describes the rotational transitions. It depends on the orientation of the molecular dipole moment p in space.

The amplitude of the radiation emitted into the direction $\boldsymbol{k}$ in space is proportional to the scalar product of $\boldsymbol{k}\cdot\boldsymbol{p}$ and the intensity is the square of this amplitude. For absorbing transitions it is proportional to the scalar product $\boldsymbol{E}\cdot\boldsymbol{p}$ of electric field amplitude and molecular dipole moment $\boldsymbol{p}$.

With the orientation angles Θ and ϕ of $\hat{\boldsymbol{p}} = \boldsymbol{p}/|\boldsymbol{p}|$ against the space-fixed axis $X; Y; Z$ we obtain the relation (Fig. 9.53)

$$\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{p} = p(\varepsilon_x\sin\Theta\cos\phi + \varepsilon_y\sin\Theta\sin\phi + \varepsilon_z\cos\Theta) \qquad (9.131a)$$

where ε_i is the ith component of $\hat{\boldsymbol{\varepsilon}} = \boldsymbol{E}/|\boldsymbol{E}|$ against the space fixed axis $i = X, Y, Z$. The angles can be expressed by the spherical surface harmonics Y^M_J:

$$\sqrt{\frac{4\pi}{3}}Y^0_1 = \cos\Theta\,; \quad \sqrt{\frac{8\pi}{3}}Y^{\pm1}_1 = \mp\sin\Theta\cdot e^{\pm i\phi} \qquad (9.131b)$$

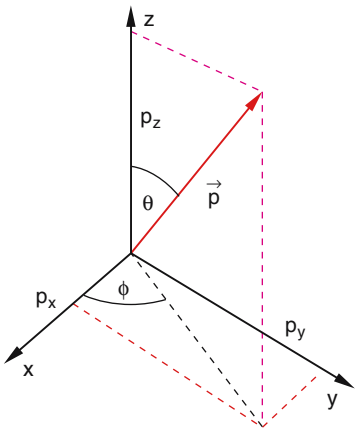


Fig. 9.53. Orientation of molecular dipole moment $\boldsymbol{p}$ in a space-fixed coordinate system

which gives

$$\hat{\boldsymbol{\varepsilon}}\cdot\boldsymbol{p} = \qquad (9.131c)$$
$$p\sqrt{\frac{4\pi}{3}}\left(\varepsilon_z Y^0_1 + \frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y^1_1 + \frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}}Y^{-1}_1\right)\,.$$

Inserting this into the second integral in (9.129) and extracting the components of the space fixed unit vector $\boldsymbol{\varepsilon}$ out of the integral gives for the angular part of the transition probability integrals of the form

$$\int Y^{M_i}_{J_i}Y^{\Delta M}_1 Y^{M_k}_{J_k}\,\mathrm{d}\Omega \quad \text{with} \quad \Delta M = 0, \pm 1$$

with the result that these integrals are always zero, except for $\Delta J = J_i - J_k = \pm 1$.

This selection rule is readily understandable, because the absorbed or emitted photon has the spin $s = \pm 1h$ and the total angular momentum of the system photon + molecule has to be conserved.

For the projection quantum number M the selection rules are analogue to that for atoms:

$\Delta M = 0$ for linear polarization of the radiation and $\Delta M = \pm 1$ for circular polarization.

Note:

The angle ϑ is measured against the molecular axis in the molecular coordinate system, while Θ and ϕ are the angles between the molecular dipole moment and the space fixed quantization axis (see above).

In order to save indices in spectroscopic literature the upper state (v_k, J_k) is always labeled with a prime as

(v', J'), whereas the lower state (v_i, J_i) is labeled with a double prime as (v'', J''). Transitions with

$$\Delta J = J' - J'' = +1$$

are called ***R-transitions***, those with

$$\Delta J = J' - J'' = -1$$

are ***P-transitions***.

All allowed rotational transitions appear in the spectrum as absorption- or emission lines (Fig. 9.54). All rotational lines of a vibrational transition form a ***vibrational band***. Its rotational structure is given by the wavenumbers of all rotational lines

$$\begin{aligned}&\overline{\nu}(v', J \leftrightarrow v'', J'') \qquad (9.132)\\ &= \overline{\nu}_0 + B'_v J'(J'+1) - D'_v J'^2 (J'+1)^2\\ &\quad - \left[B''_v J''(J''+1) - D''_v J''^2 (J''+1)^2\right]\end{aligned}$$

where ν_0 is the ***band origin***. It gives the position of a fictious Q-line with $J' = J'' = 0$. Since this line does not exist in rotational-vibrational spectras of diatomic molecules, there is a missing line at $\nu = \nu_0$ (Fig. 9.54).

Since the rotational constant $B_v = B_e - \alpha_e(v + \frac{1}{2})$ generally decreases with increasing v ($\alpha_e > 0$ for most molecules) it follows that $B'_v < B''_v$. Plotting $\nu(J = J'')$ for P- and R transitions as a function of ν gives the *Fortrat-diagram* shown in Fig. 9.55. The R-lines are on the high frequency side of the band origin ν_0 while the P lines are on the low frequency side. In Fig. 9.56 the vibration-rotation spectrum of HCl is shown with the P- and R-branch. The lines are split into two components, because the absorbing gas was a mixture of the two isotopomers of HCl with the two atomic isotopes ^{35}Cl and ^{37}Cl. Since the rotational and vibrational constants depend on the reduced mass M the lines of different isotopomers are shifted against each other.

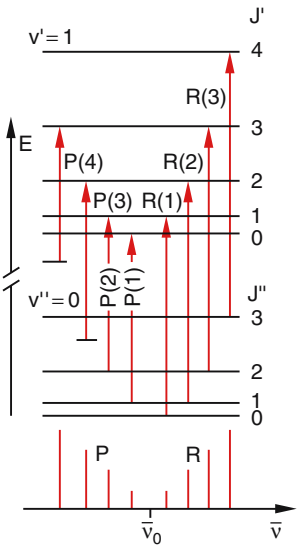


Fig. 9.54. P and R rotational transitions between the vibrational levels $v'' = 0$ and $v' = 0$

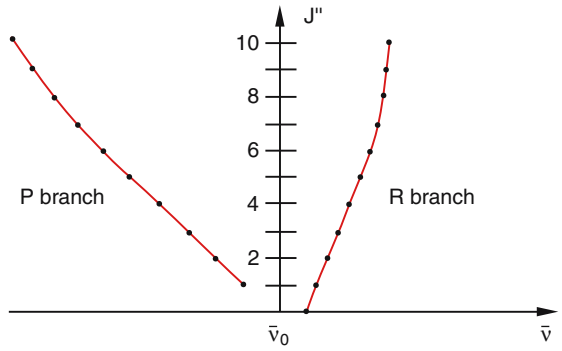


Fig. 9.55. Fortrat diagram of the P- and R-branch of vibrational-rotational transitions

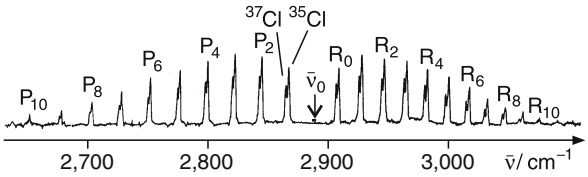


Fig. 9.56. Vibrational-rotational absorption of the $H^{35}Cl$ and $H^{37}Cl$ isotopomers in the infrared region between $\lambda = 3.3-3.7\,\mu m$

9.6.3 The Structure of Electronic Transitions

We will now evaluate the matrix element (9.125) for electronic transitions. The electronic part $M^{el}_{ik}(R)$ depends on the internuclear distance R, because the electronic wave functions Φ depend parametrically on R. In many cases the dependence on R is weak and we can expand $M^{el}_{ik}(R)$ into a Taylor series

$$\boldsymbol{M}^{el}_{ik}(R) = \boldsymbol{M}_{ik}(R_e) + \left(\frac{d\boldsymbol{M}^{el}_{ik}}{dR}\right)_{R_e} (R - R_e) + \ldots . \qquad (9.133)$$

In a first approximation only the first term, independent of R, is considered, which can be regarded as an average

of $M_{ik}(R)$ over the range of R-values covered by the vibrating molecule. In this case the constant $M_{ik}(R_e)$ can be put before the integral over the nuclear coordinates. Using the normalized nuclear wave functions $\chi_N = S(R) \cdot Y(\vartheta, \varphi)$ and the vibrational wave functions $\psi_{vib} = R \cdot S(R)$ the matrix element becomes

$$\boldsymbol{M}_{ik} = \boldsymbol{M}_{ik}^{el} \int \psi_{vib}^{*}(v_i)\psi_{vib}(v_k)\,\mathrm{d}R \cdot \int Y_{J_i}^{M_i} Y_{J_k}^{M_k} \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi \qquad (9.134)$$

where Mh is the projection of the rotational angular momentum $\boldsymbol{J}$ onto a selected axis (for instance, in the direction of the $\boldsymbol{E}$-vector or the $\boldsymbol{k}$-vector of the incident electromagnetic wave for absorbing transitions, or in the direction from the emitting molecule to the observer for fluorescent transitions).

Note:

This approximation of an electric transition dipole moment independent of R is, for many molecules with a strong dependence $M_{ik}^{el}(R)$, too crude (Fig. 9.57). In such cases the second term in the expansion (9.133) has to be taken into account.

Since the probability of spontaneous emission is proportional to the square $|M_{ik}|^2$, the intensity of a spectral emission line

$$I(n_i, v_i, J_i \leftrightarrow n_k, v_k, J_k) \propto \left|M_{ik}^{el}\right|^2 \cdot FCF(v_i, v_k) \cdot HL(J_i, J_k) \qquad (9.135)$$

is determined by three factors.

The electronic part $|M_{ik}^{el}|^2$ gives the probability of an electron jump from the electronic state $|i\rangle$ to $|k\rangle$. It depends on the overlap of the electronic wave functions Φ_i and Φ_k and their symmetries.

The Franck–Condon factor

$$FCF(v_i, v_k) = \left| \int \psi_{vib}(v_i) \cdot \psi_{vib}(v_k)\,\mathrm{d}R \right|^2 \qquad (9.136)$$

is determined by the square of the overlap integral of the vibrational wave functions $\psi_{vib}(v_i)$ and $\psi_{vib}(v_k)$ in the upper and lower electronic state.

The Hönl–London factor

$$HL(J_i, J_k) = \left| \int Y_{J_i}^{M_i} Y_{J_k}^{M_k} \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi \right|^2 \qquad (9.137)$$

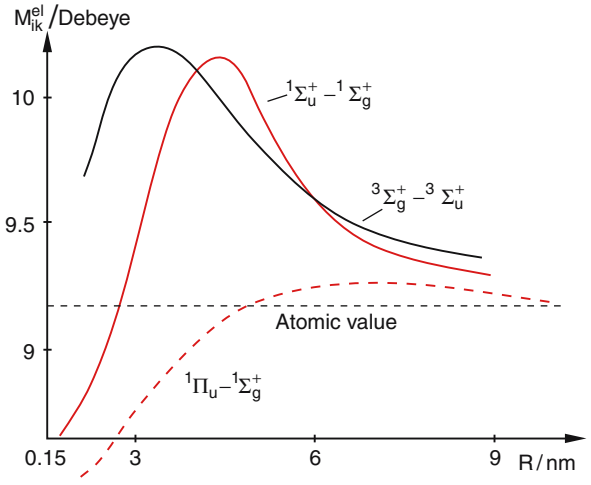


Fig. 9.57. Dependence of electronic transition dipole on internuclear distance R for several transitions of the Na_2 molecule

depends on the rotational angular momenta and their orientation in space. This factor determines the spatial distribution of the emitted radiation.

An electric dipole transition in fluorescence can only take place if none of these three factors is zero.

The probability of *absorbing transitions* depends according to (9.119b) on the scalar product of the electric field vector $\boldsymbol{E}$ and the dipole moment $\boldsymbol{p}$

$$P_{ik} \propto |\boldsymbol{E} \cdot \boldsymbol{M}_{ik}|^2 .$$

Since only the last factor in (9.135) depends on the orientation of the molecule in space, i.e., the direction of M_{ik} against the electric field vector $\boldsymbol{E}$, only the Hönl–London factor differs for spontaneous emission and absorbing transitions. For the intensity $I = \varepsilon_0 E^2$ of the incident electromagnetic wave we obtain with $\boldsymbol{E} = \boldsymbol{\varepsilon} \cdot |\boldsymbol{E}|$ the transition probability

$$\mathcal{P}_{ik} = \varepsilon_0 E^2 \cdot \left|M_{ik}^{el}(R_e)\right|^2 \times \left| \int \psi_{vib}^{v_i} \cdot \psi_{vib}^{v_k} \cdot \mathrm{d}R \right|^2 \times \left| \int Y_{J_i}^{M_i} \hat{\varepsilon} \cdot \hat{p} Y_{J_k}^{M_k} \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi \right|^2 . \qquad (9.138)$$

a) The General Structure of Electronic Transitions

Molecular electronic spectra have structures as shown in (Fig. 9.58).

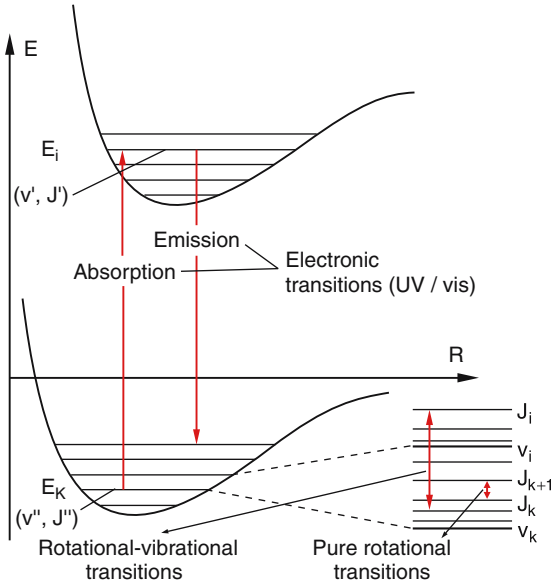


Fig. 9.58. Schematic representation of the structure of molecular transitions

All allowed transitions $J_i'' \longleftrightarrow J_k'$ between the rotational levels J_k' of a given vibrational level v' in the upper electronic state and J_i'' of v'' in the lower electronic state form a *band*. In absorption or fluorescence spectra such a band consists of many rotational lines.

Transitions with $\Delta J = 0$ form the **Q-*branch***, those with $\Delta J = J_k' - J_i'' = +1$ the **R-*branch*** and with $\Delta J = -1$ the **P-*branch***. Q-branches are only present in transitions where the electronic angular momentum changes by $1h$, (e. g., for $\Sigma \leftrightarrow \Pi$ transitions) in order to compensate for the spin of the absorbed or emitted photon. Electronic transitions with $\Delta\Lambda = 0$ (e. g., between two Σ-states) have only P and R branches.

The total system of all vibrational bands of this electronic transition is called a *band system*. The total number of lines in such a band system depends not only on the transition probabilities but also on the number of populated levels in the lower or upper electronic state.

The intensities of the lines in the *emission spectrum* are proportional to the population of the emitting upper levels and to the transition probability A_{ik}:

$$I_{ik}^{\text{em}} = g_k N_k A_{ik} \tag{9.139a}$$

where $g_k = (2J_k + 1)$ is the statistical weight of the level. The number of emitting levels depends on the excitation mechanism. Generally, the energy of the upper electronic state is for $T = 300\,\text{K}$ large compared to the thermal energy kT. Therefore the thermal population is negligible. Optical pumping with lasers allows the population of single selected levels. In this case the fluorescence spectrum becomes very simple because it is emitted from a single upper level. In gas discharges, many upper levels are excited by electron impact and the number of lines in the emission spectrum becomes very large.

The *absorption spectrum* consists of all allowed transitions from populated lower levels.

Their intensity, as given in Sect. 7.2, is given by

$$I_{ik}^{\text{abs}} = g_i N_i w(\nu) B_{ik} \,. \tag{9.139b}$$

At thermal equilibrium the population distribution follows a Boltzmann distribution

$$N_i = g_i \, \mathrm{e}^{-E_i/kT} \,. \tag{9.140}$$

b) The Rotational Structure of Electronic Transitions

The wavenumnber of a rotational line in the electronic spectrum of a diatomic molecule corresponding to a transition $(n_i, v_i, J_i) \leftrightarrow (n_k, v_k, J_k)$ is

$$\begin{aligned}\overline{\nu}_{ik} = {} & (T_e' - T_e'') + \left(T_{\text{vib}}(v') - T_{\text{vib}}(v'')\right) \\ & + \left(T_{\text{rot}}(J') - T_{\text{rot}}(J'')\right)\end{aligned} \tag{9.141}$$

where T_e gives the minimum of the potential curves $E_{\text{pot}}(R)$ of the electronic states $|i\rangle$ or $|k\rangle$, T_{vib} is the term value of the vibrational state for $J = 0$ and $T_{\text{rot}}(J)$ the pure rotational term value.

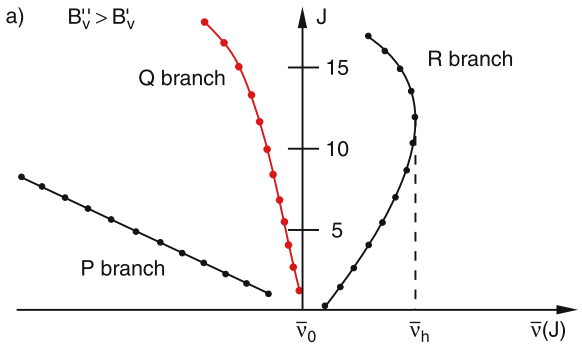
The rotational structure of a vibrational band is then (similarly to the situation for vibrational–rotational transitions within the same electronic state) given by

$$\begin{aligned}\overline{\nu}_{ik} = {} & \overline{\nu}_0(n_i, n_k, v_i, v_k) + B_v' J'(J'+1) \\ & - D_v' J'^2 (J'+1)^2 \\ & - \left[B_v'' J''(J''+1) - D_v'' J''^2 (J''+1)^2\right] \,.\end{aligned} \tag{9.142}$$

In contrast to (9.132), the rotational constant B_v' in the upper state can now either be larger or smaller than B_v'' in the lower electronic state. This depends on the binding energies and the equilibrium distances R_e in the two states. The ***Fortrat-Diagrams*** shown in Fig. 9.59 has a different structure for each of the two cases.

At those J-values where the curve $\nu(J)$ becomes vertical, the density of rotational lines within a given spectral interval has a maximum. The derivative $d\nu/dJ$ changes its sign. For the case $B''_v > B'_v$ the positions $\nu(J)$ of the rotational lines increase for R-lines before the maximum and then decrease again (Fig. 9.59a). The position ν_h of this line pileup is called the ***band head***. For $B''_v > B'_v$ the R-lines show a band head at the high frequency side of the band, while for $B''_v < B'_v$ the P-lines accumulate in a band head at the low frequency side (Fig. 9.59b). The line density may become so high, that even with very high spectral resolution the different lines cannot be resolved. This is illustrated by Fig. 9.60, which shows the rotational lines in the electronic transition of the Cs_2 molecule around the band head, taken with sub-Doppler resolution.

In molecular electronic spectra taken with photographic detection and medium resolution where only part of the rotational lines are resolved, a sudden jump of the blackening on the photoplate appears at the band head



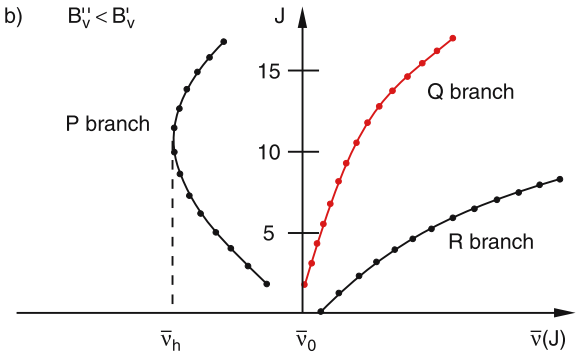


Fig. 9.59a,b. Fortrat-diagram for P, Q and R branches in electronic transitions: (**a**) $B''_v > B'_v$ (**b**) $B''_v < B'_v$

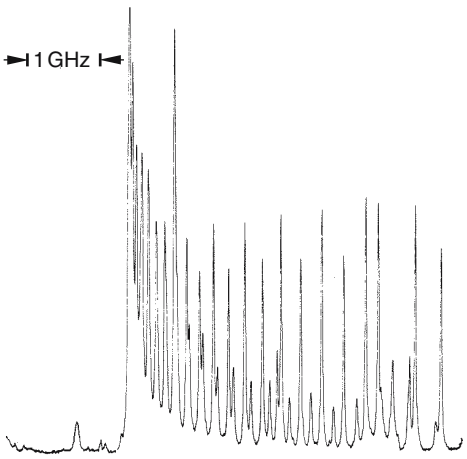


Fig. 9.60. Band head of the vibrational band $v' = 9 \leftarrow v'' = 14$ of the electronic transition $C\,^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ of the Cs_2 molecule, recorded with sub-Doppler-resolution

while the line density gradually decreases with increasing distance from the band head. The band appears shadowed (Fig. 9.61) to the opposite frequency side of the band head. For $B''_v > B'_v$ the band is red-shadowed and the band head is on the blue side of the band, while for $B''_v < B'_v$ the band is blue-shadowed and the band head appears on the red side.

In cases where the electronic transition allows Q-lines, their spectral density is higher than that of the P- and R-lines. For $B'_v = B''_v$ all Q-lines $Q(J)$ have the same position. For $B'_v > B''_v$ their positions $\nu(J)$ increase with increasing J (Fig. 9.59a) while for $B'_v < B''_v$ they decrease (Fig. 9.59b).

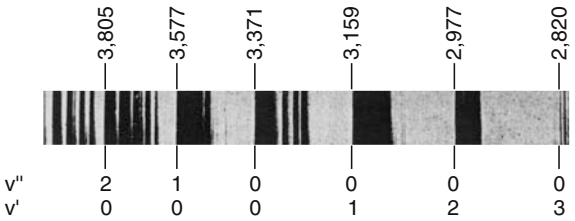


Fig. 9.61. Photographic recording of the band structure in the electronic transition $3\Pi_g \leftarrow 3\Pi_u$ of the N_2 molecule. The wavelengths of the band heads are given in Å = 0.1 nm above the spectrum (with the kind permission of the late Prof. G. Herzberg [G. Herzberg: Molecular Spectra and Molecular Structure Vol. I (van Nostrand, New York, 1964)])

c) The Vibrational Structure and the Franck–Condon Principle

The vibrational structure of electronic transitions is governed by the Franck–Condon factor (9.136), which in turn depends on the overlap of the vibrational wave functions in the two electronic states. In a classical model, which gives intuitive insight into electronic transitions, the absorption or emission of a photon occurs within a time interval that is short compared to the vibrational period T_{vib} of the molecule. In a potential diagram (Fig. 9.62) the electronic transitions between the two states can be then represented by vertical arrows. This means, that the internuclear distance R is the same for the starting point and the final point of the transition. Since the momentum $p = h\nu/c$ of the absorbed or emitted photon is very small compared to that of the vibrating nuclei, the momentum p of the nuclei is conserved during the electronic transition. Also, the kinetic energy $E_{\text{kin}} = p^2/2M$ does not change. From the energy balance

$$\begin{aligned} h\nu &= E'(v') - E''(v'') \\ &= E'_{\text{pot}}(R) + E'_{\text{kin}}(R) - [E''_{\text{pot}}(R) + E''_{\text{kin}}(R)] \\ &= E'_{\text{pot}}(R^*) - E''_{\text{pot}}(R^*) \end{aligned} \tag{9.143}$$

it follows that the electronic transition takes place at a nuclear distance R^* where the kinetic energies of the vibrating nuclei in the upper and lower state are equal, i.e., $E'_{\text{kin}}(R^*) = E''_{\text{kin}}(R^*)$. This can be graphically illustrated by the difference potential

$$U(R) = E''_{\text{pot}}(R) - E'_{\text{pot}}(R) + E(v') \tag{9.144}$$

introduced by *Mulliken* (Fig. 9.63). The electron jump from one electronic state into the other takes place at such a value R^*, where Mulliken's difference potential intersects the horizontal energy line $E = E(v'')$, where

$$U(R^*) = E(v'') \,.$$

In the quantum mechanical model, the probability for a transition $v' \leftrightarrow v''$ is given by the Franck–Condon factor (9.136). The ratio

$$\mathcal{P}(R)\,\mathrm{d}R = \frac{\psi'_{\text{vib}}(R)\psi''_{\text{vib}}(R)\,\mathrm{d}R}{\int \psi'_{\text{vib}}(R)\psi''_{\text{vib}}(R)\,\mathrm{d}R} \tag{9.145}$$

gives the probability that the transition takes place in the interval $\mathrm{d}R$ around R. It has a maximum for $R = R^*$.

If the two potential curves $E'_{\text{pot}}(R)$ and $E''_{\text{pot}}(R)$ have a similar R-dependence and equilibrium distances $R'_{\text{e}} \approx R''_{\text{e}}$ the FCF for transitions with $\Delta v = 0$ are maximum and for $\Delta v \neq 0$ they are small (Fig. 9.62a).

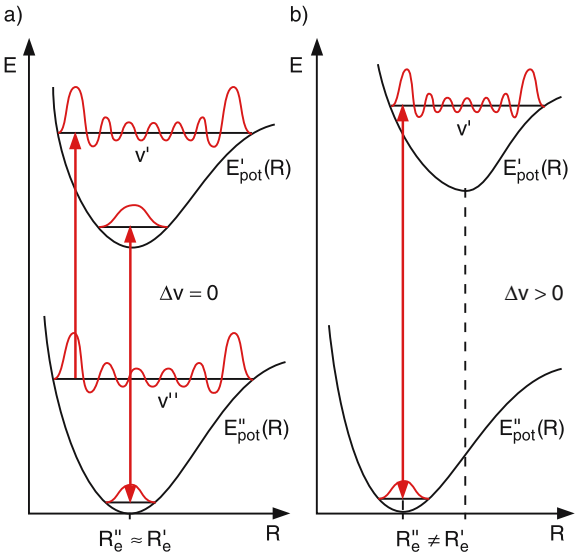


Fig. 9.62. Illustration of the Franck-Condon principle for vertical transitions with $\Delta v = 0$ (**a**) and $\Delta v > 0$ in case of potential curves with $R''_{\text{e}} = R'_{\text{e}}$ and $R'_{\text{e}} > R''_{\text{e}}$

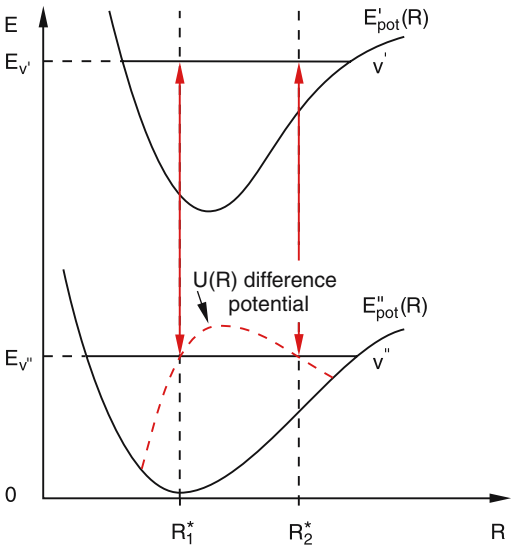


Fig. 9.63. Illustration of the Mulliken-difference potential $V(R) = E''_{\text{pot}}(R) - E'_{\text{pot}}(R) + E(v')$

The larger the shift $\Delta R = R'_e - R''_e$ the larger becomes the difference Δv for maximum FCF (Fig. 9.62b).

9.6.4 Continuous Spectra

If absorption transitions lead to energies in the upper electronic state above its dissociation energy, unbound states are reached with non-quantized energies. The absorption spectrum then no longer consists of discrete lines but shows a continuous intensity distribution $I(\nu)$. A similar situation arises, if the energy of the upper state is above the ionization energy of the molecule, similarly to atoms (see Sect. 7.6).

In the molecular spectra the ionization continuum is, however, superimposed by many discrete lines that correspond to transitions into higher vibrational-rotational levels of bound Rydberg states in the neutral electron. Although the electronic energy of these Rydberg states is still below the ionization limit, the additional vibrational-rotational energy brings the total energy above the ionization energy of the non-vibrating and non-rotating molecule (Fig. 9.64).

Such states can decay by autoionization into a lower state of the molecular ion, where part of the kinetic energy of the vibrating and rotating molecular core is transferred to the Rydberg electron, which then gains sufficient energy to leave the molecule (Fig. 9.65). The situation is similar to that in doubly excited Rydberg atoms where the energy can be transferred from one excited electron to the Rydberg electron (see Sect. 6.6.2). However, while this process in atoms takes place within $10^{-13}-10^{-15}$ s, due to the strong electron-electron interaction, in molecules it is generally very slow (between $10^{-6}-10^{-10}$ s), because the coupling between the motion of the nuclei and the electron is weak. In fact, within the adiabatic approximation it would be zero! The vibrational or rotational autoionization of molecules represent a breakdown of the Born–Oppenheimer approximation. The decay of these levels by autoionization is slow and the lines appear sharp. In Fig. 9.65 an example of the excitation scheme of autoionizing Rydberg levels is shown. The Rydberg levels are generally excited in a two-step process from the ground state $|g\rangle$ to level $|i\rangle$ by absorption of a photon from a laser and the further excitation $|i\rangle \rightarrow |k\rangle$ by a photon from another laser. The autoionization of the Rydberg level $|k\rangle$ is monitored by observation of the resultant molecular ions. A section of the autoionization spectrum of the Li_2-molecule with sharp lines and a weak continuous background, caused by direct photoionization, is shown in Fig. 9.66. The lines have an asymmetric line profile called a ***Fano-profile*** [9.11]. The reason for this asymmetry is an interference effect between two possible excitation paths to the energy E^* in the ionization continuum, as illustrated in Fig. 9.67:

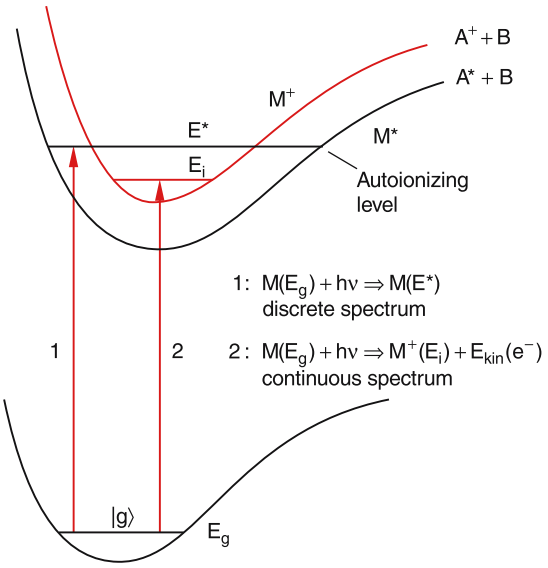


Fig. 9.64. Excitation (1) of a bound Rydberg level in the neutral molecule and (2) of a bound level in the molecular ion M^+

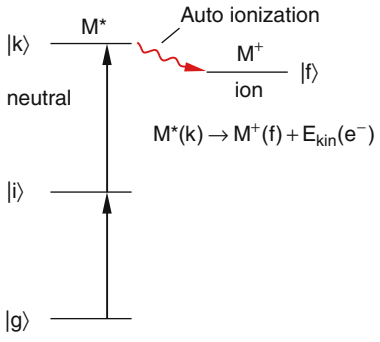


Fig. 9.65. Two-step excitation of a molecular Rydberg level $|k\rangle$, which transfers by auto ionization into a lower level $|f\rangle$ of the molecular ion. The difference energy is given to the free electron

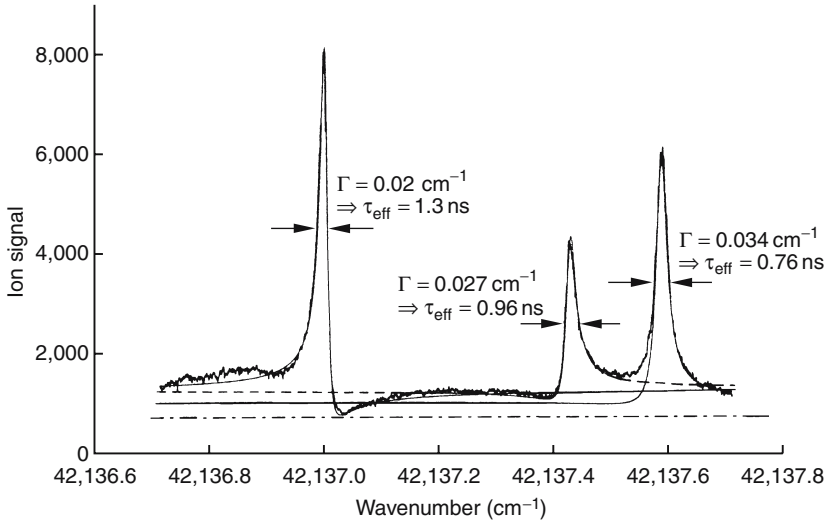


Fig. 9.66. Section of the auto ionization spectrum of the Li_2 molecule

1. The excitation of the Rydberg level $|k\rangle$ of the neutral molecule from level $|i\rangle$ with the probability amplitude D_1 with subsequent autoionization,
2. The direct photoionization from level $|i\rangle$ with the probability amplitude D_2.

When the frequency of the excitation lasers is tuned, the phase of the transition matrix element does not change much for path 2, but much more for path 1, because the frequency is tuned over the narrow resonance of a discrete transition. The total transition probability

$$\mathcal{P}_{if} = |D_1 + D_2|^2$$

therefore changes with the frequency of the excitation laser because the interference is on one side of the resonance destructive on the other constructive, resulting in an asymmetric line profile.

Continuous spectra can also appear in emission, if a bound upper level is excited that emits fluorescence into a repulsive lower state. Such a situation is seen in excimers, which have stable excited upper states but an unstable ground state (Fig. 9.68). For illustration, the emission spectrum of an excited state of the NaK alkali molecule is shown in Fig. 9.69. This state is a mixture of

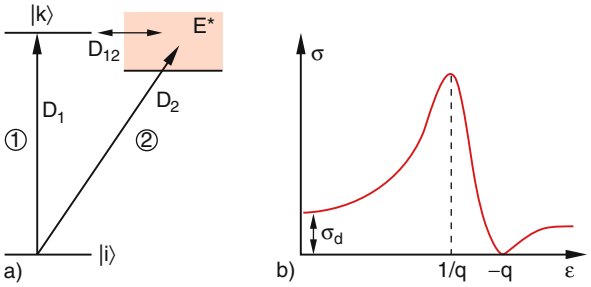


Fig. 9.67. (**a**) Interference of two possible excitation pathways to the energy E^* in the ionization continuum (**b**) Resultant Fano-profile with asymmetric line shape. σ_d is the absorption crosssection for direct photoionization

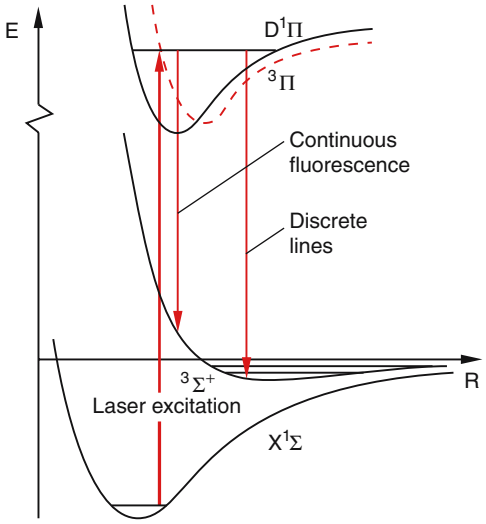


Fig. 9.68. Level scheme of the NaK molecule with excitation and discrete and continuous emission spectrum

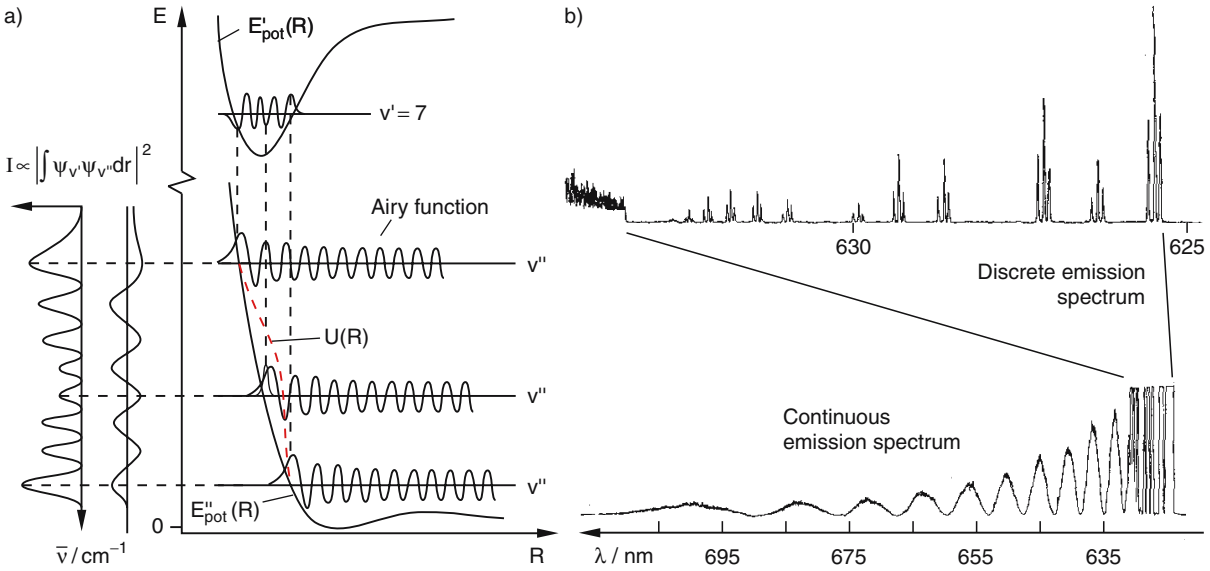


Fig. 9.69. (**a**) Vibrational overlap and Franck-Condon factor for the continuous emission (**b**) Measured emission spectrum of the NaK molecule

a singlet and a triplet state, due to strong spin-orbit coupling. Therefore transitions from this mixed state into lower singlet as well as triplet states becomes allowed. While the emission into the stable singlet ground state $X\,^1\Sigma$ shows discrete lines, the emission into the weakly bound lowest triplet state $3\,^3\Sigma$ shows, on the short wavelength side, a section of discrete lines terminating at bound vibrational-rotational levels in the shallow potential well of the $a\,^3\Sigma$ state and, on the long wavelength side, a modulated continuum terminating on energies above the dissociation limit of the $a\,^3\Sigma$ state. The intensity modulation reflects the FCF, i. e., the square of the overlap integral between the vibrational wave function of the bound level in the upper electronic state with the function of the unstable level in the repulsive potential above the dissociation energy of the lower state which can be described by an Airy function. The frequency $\nu = E'(R) - E''(R)$ and the wavelength $\lambda = c/\nu$ of the emission depends on the internuclear distance R because the emission terminates on the Mulliken potential of the repulsive lower state (dashed blue curve in Fig. 9.69). The number $q = v' - 1$ of nodes in the fluorescence spectrum gives the vibrational quantum number v' of the emitting level.

SUMMARY

- For the simplified model of a rigid diatomic molecule, the electronic wave functions $\psi(r, R)$ and the energy eigenvalues $E(R)$ can be approximately calculated as a function of the internuclear distance R. The wave functions are written as a linear combination of atomic orbitals (LCAO approximation) or of other suitable basis functions.
- In a rotating and vibrating molecule the kinetic energy of the nuclei is generally small compared to the total energy of a molecular state. This allows the separation of the total wave function $\psi(r, R) = \chi_N(R)\Phi^{el}(r, R)$ into a product of a nuclear wave function $\chi(R)$ and an electronic function $\Phi^{el}(r, R)$, which depends on the electronic coordinates r and only contains R as a free parameter. This approximation, called the adiabatic or *Born–Oppenheimer approximation*, neglects the coupling between nuclear and electron motion. The potential equals that of the rigid molecule and the vibration and rotation takes place in this potential.
- Within this approximation the total energy of a molecular level can be written as the sum $E = E_{el} + E_{vib} + E_{rot}$ of electronic, vibrational and rotational energy. This sum is independent of the nuclear distance R.
- The electronic state of a diatomic molecule is characterized by its symmetry properties, its total energy E and by the angular momentum and spin quantum numbers. For one-electron systems these are the quantum numbers $\lambda = l_z/h$ and $\sigma = s_z/h$ of the projections l_z of the electronic orbital angular momentum and s_z of the spin s onto the internuclear z-axis. For multi-electron systems $L = \Sigma l_i$, $S = \Sigma s_i$, $\Lambda = L_z/h = \Sigma\lambda_i$, and $M_s = \Sigma\sigma_i = S_z/h$. Although the vector $\boldsymbol{L}$ might depend on R, the projection L_z does not.
- The potential curves $E_{pot}(R)$ are the sum of mean kinetic energy $\langle E_{kin}\rangle$ of the electrons, their potential energy and the potential energy of the nuclear repulsion. If these potential curves have a minimum at $R = R_e$, the molecular state is stable. The molecule vibrates around the equilibrium distance R_e. If $E_{pot}(R)$ has no minimum, but monotonically decreases with increasing R the state is unstable and it dissociates.
- The vibration of a diatomic molecule can be described as the oscillation of one particle with reduced mass $M = M_A M_B/(M_A + M_B)$ in the potential $E_{pot}(R)$. In the vicinity of R_e the potential is nearly parabolic and the vibrations can be well-approximated by a harmonic oscillator. The allowed energy eigenvalues, defined by the vibrational quantum number v, are equidistant with a separation $\Delta E = \hbar\omega$. For higher vibrational energies the molecular potential deviates from a harmonic potential. The distances between vibrational levels decrease with increasing energy. A good approximation to the real potential is the Morse-potential, where ΔE_{vib} decreases linearly with energy. Each bound electronic state has only a finite number of vibrational levels.
- The rotational energy of a diatomic molecule $E_{rot} = J(J+1)h^2/2I$ is characterized by the rotational quantum number J and the moment of inertia $I = MR^2$. Due to the centrifugal force F_c the distance R increases slightly with J until F_c is compensated by the restoring force $F_r = -dE_{pot}/dR$ and the rotational energy becomes smaller than that of a rigid molecule.
- The absorption or emission spectra of a diatomic molecule consists of:
  a) Pure rotational transitions within the same vibrational level in the microwave region
  b) Vibrational-rotational transitions within the same electronic state in the infrared region
  c) Electronic transitions in the visible and UV region
- The intensity of a spectral line is proportional to the product $N \cdot |M_{ik}|^2$ of the population density N in the absorbing or emitting level and the square of the matrix element M_{ik}.
- Homonuclear diatomic molecules have neither a pure rotational spectrum nor a vibrational-rotational spectrum. They therefore do not absorb in the microwave and the mid-infrared region, unless transitions between close electronic states fall into this region.

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- The electronic spectrum consists of a system of vibrational bands. Each vibrational band includes many rotational lines. Only rotational transitions with $\Delta J = 0; \pm 1$ are allowed. The intensity of a rotational transition depends on the Hönl-London factor and those of the different vibrational bands are determined by the Franck-Condon factors, which are equal to the square of the vibrational overlap integral.
- Continuous absorption spectra arise for transitions into energy states above the dissociation energy or above the ionization energy. Continuous emission spectra are observed for transitions from bound upper states into a lower state with a repulsive potential.

PROBLEMS

1. How large is the Coulomb repulsion of the nuclei in the H_2^+ ion and the potential energy of the electron with wave function $\Phi^+(r, R)$ at the equilibrium distance $R_e = 2a_0$? First calculate the overlap integral $S_{AB}(R)$ in (9.13) with the wave function (9.9). What is the mean kinetic energy of the electron, if the binding energy is $E_{pot}(R_e) = -2.65\,\text{eV}$? Compare the results with the corresponding quantities for the H atom.
2. How large is the electronic energy of the H_2 molecule (without nuclear repulsion) for $R = R_e$ and for the limiting case $R = 0$ of the united atom?
3. a) Calculate the total electronic energy of the H_2 molecule as the sum of the atomic energies of the two H atoms minus the binding energy of H_2. b) Compare the vibrational and rotational energy of H_2 at a temperature $T = 300\,\text{K}$ with the energy of the first excited electronic state of H_2.
4. Prove that the two separated equations (9.75) are obtained when the product ansatz (9.74) is inserted into the Schrödinger equation (9.73).
5. Show that the energy eigenvalues (9.104) are obtained when the Morse potential (9.103) is inserted into the Schrödinger equation (9.80).
6. What is the ionization energy of the H_2 molecule when the binding energies of H_2 and H_2^+ are $E_B(H_2) = -4.48\,\text{eV}$ and $E_B(H_2^+) = -2.65\,\text{eV}$ and the ionization energy of the H atom $E_{Io} = 13.6\,\text{eV}$?
7. Calculate the frequencies and wavelengths for the rotational transition $J = 0 \rightarrow J = 1$ and $J = 4 \rightarrow J = 5$ for the HCl molecule. The internuclear distance is $R_e = 0.12745\,\text{nm}$. What is the frequency shift between the two isotopomers $H^{35}Cl$ and $H^{37}Cl$ for the two transitions? What is the rotational energy for $J = 5$?
8. If the potential of the HCl molecule around R_e is approximated by a parabolic potential $E_{pot} = k(R - R_e)^2$ a vibrational frequency $\nu_0 = 9 \times 10^{13}\,\text{s}^{-1}$ is obtained. What is the restoring force constant k? How large is the vibrational amplitude for $v = 1$?