
12. Raman Spectra

Along with infra-red spectroscopy and microwave spectroscopy, a further important method of investigating the rotational and vibrational spectra of molecules is *Raman spectroscopy*. It is based on the inelastic scattering of light from molecules, which is known as the Raman effect. The rotational and vibrational frequencies of the molecules which scatter the light are present in the scattered spectrum as difference frequencies relative to the elastically-scattered primary light. In this chapter, we shall explain how this scattered-light spectrum arises and what information it contains (Sects. 12.1–12.3). In the final section, 12.4, we then discuss the statistics of nuclear spin states and their influence on the rotational structure of the spectrum. This last section refers not only to the Raman effect, but also to rotational spectra in general, and can thus be regarded as a complement to Chap. 9.

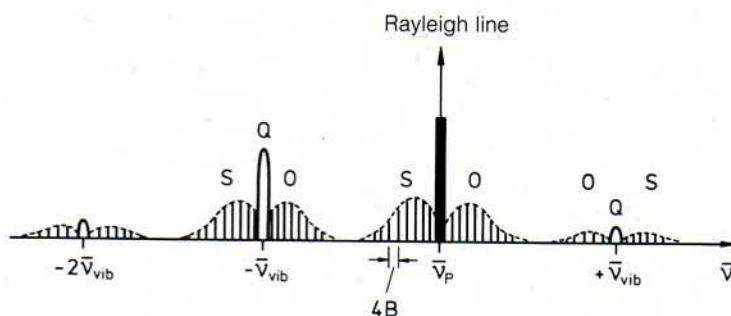
12.1 The Raman Effect

As we have already seen, light can be emitted or absorbed by molecules, if the resonance condition $\Delta E = h\nu$ is fulfilled. In addition, however, as we know from classical physics, light of any wavelength can be scattered. Elastic or Rayleigh scattering, as described by classical physics, is explained in terms of the force acting on the electronic shells of the molecule due to the \mathbf{E} vector of the light. This force induces an electric dipole moment $\mathbf{p}_{\text{ind}} = \alpha\mathbf{E}$, which oscillates at the frequency of the light and, acting as a Hertzian dipole, emits on its own part a light wave of the same frequency. This scattered radiation is coherent with the radiation field which induces it.

In the year 1928, *Raman* observed frequency-shifted lines in the spectrum of scattered light. The frequency shift relative to the primary light corresponded to the vibrational and rotational frequencies of the scattering molecules. This process, which had been predicted theoretically by *Smekal* in 1925, is called the Raman effect and forms the basis of Raman spectroscopy. The Raman-scattered light, in contrast to Rayleigh scattering, is not coherent with the primary light. Frequency shifts to smaller energies (Stokes lines) as well as shifts to higher energies (anti-Stokes lines) are observed. The frequency shift is independent of the frequency of the primary light and is a unique property of the scattering molecules. The entire Raman spectrum of a molecule is shown schematically in Fig. 12.1. It is the structure of this spectrum which we want to elucidate.

To observe the Raman spectrum, a high spectral resolution is required, owing to the smallness of the frequency shifts. The order of magnitude of these shifts is 1 cm^{-1} in the rotational Raman effect. Using primary light in the visible range, with a wavenumber $\bar{\nu}_p$ (p stands for primary) of the order of $20\,000 \text{ cm}^{-1}$, we also need to suppress the unshifted and many times more intense elastically scattered light in order to observe these small shifts;

Fig. 12.1. The total Raman spectrum of a diatomic molecule, represented schematically. The Rayleigh line at the frequency $\bar{\nu}_p$ of the primary light is surrounded directly by the rotational Raman lines. Spaced at frequency shifts corresponding to the molecular vibrations, $\bar{\nu}_{vib}$, are the rotational-vibrational Raman lines, the *Q*, *S*, and *O* branches. The corresponding anti-Stokes lines at $\bar{\nu}_p + \bar{\nu}_{vib}$ are much weaker and usually cannot be observed. The same is true of the harmonics at $2\bar{\nu}_{vib}$



for this reason, a double or even a triple monochromator is often used for the detected beam. Furthermore, the smallest possible linewidth of the primary light is also necessary; otherwise, it is impossible to separate the weak Raman-scattered lines from the Rayleigh line, which is orders of magnitude more intense. For this reason, laser light is often used as the primary light source in Raman measurements. As is well known, lasers can be used to produce very intense monochromatic beams of light, with linewidths much smaller than the expected Raman shifts. Figure 12.2 gives a schematic drawing of a typical experimental set-up.

12.2 Vibrational Raman Spectra

We at first leave the molecular rotations out of consideration and assume that the molecule exhibits only vibrations. In the case of free molecules, we must naturally later revise this assumption.

The *classical* explanation of the *vibrational Raman effect* begins with the explanation of Rayleigh scattering. In this theory, it is assumed that the scattering molecule initially is not vibrating or rotating. When primary light of frequency ν_p (also denoted by ν_0) and an electric field strength $E = E_0 \cos(2\pi \nu_p t)$ strikes the molecule, a dipole moment is induced in its electronic shells, which oscillates with the same frequency ν_p as the E vector of the primary light. We then have

$$p(t) = \alpha E_0 \cos(2\pi \nu_p t) . \quad (12.1)$$

If, on the other hand, the molecule is already vibrating at one of its characteristic vibrational frequencies, then the oscillations of the induced moment are amplitude modulated at the frequency ν_{vib} of the molecular vibration, assuming that the polarisability α of the molecule changes as a function of the internuclear distance R of the vibrating atomic nuclei. The polarisability can be expanded as a series in powers of the internuclear distance R :

$$\alpha(R) = \alpha(R_0) + \frac{d\alpha}{dR}(R - R_0) + \text{higher order terms} . \quad (12.2)$$

Due to the molecular vibrations, R is time-dependent. It obeys the equation:

$$R = R_0 + q \cos(2\pi \nu_{vib} t) . \quad (12.3)$$

Combining this equation with (12.2), we find

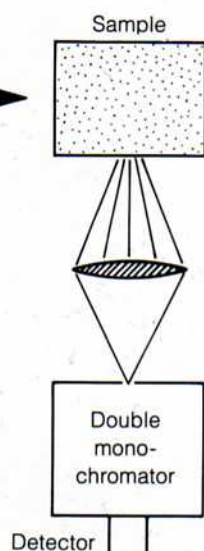


Fig. 12.2. An experimental set-up for observing the Raman effect. Detection is carried out preferentially perpendicular to the direction of the incoming primary light beam, in order to keep the intensity of the primary light in the detector as small as possible

$$p(t) = \alpha E = \left[\alpha(R_0) + \frac{d\alpha}{dR} q \cos(2\pi \nu_{\text{vib}} t) \right] E_0 \cos(2\pi \nu_p t), \quad (12.4)$$

or, rewriting using well-known trigonometric identities,

$$p(t) = \alpha(R_0) E_0 \cos(2\pi \nu_p t) + \frac{d\alpha}{dR} E_0 q \{ \cos[2\pi(\nu_p + \nu_{\text{vib}})t] + \cos[2\pi(\nu_p - \nu_{\text{vib}})t] \}. \quad (12.5)$$

In this way, sidebands are produced in the scattered light spectrum, having the frequencies $\nu_p \pm \nu_{\text{vib}}$.

This is the 1st order vibrational Raman effect. With decreasing intensity, one can also observe Raman lines with $\nu_p \pm 2\nu_{\text{vib}}$, $\nu_p \pm 3\nu_{\text{vib}}$, etc. due to the ever-present anharmonicity, i.e. the terms of higher order in the series expansion of $\alpha(R)$ in (12.2). These are called the Raman effect of second, third, ... order.

A vibration is thus Raman-active if $d\alpha/dR \neq 0$, that is, the polarisability α of the molecule must change as a function of the internuclear distance R during a vibration. This is always the case for diatomic molecules. For this reason, homonuclear and thus nonpolar molecules such as H_2 or N_2 are Raman-active. Their rotational and vibrational spectra can be measured using the Raman effect, although they are not accessible to microwave or infra-red spectroscopies because the transitions are forbidden by symmetry.

In the case of polyatomic molecules with centres of inversion, infra-red and Raman spectroscopies complement each other when one wishes to observe the molecular vibrations. In such molecules, the infra-red active normal modes are Raman-inactive, and the infra-red forbidden normal modes are Raman-allowed. This can be illustrated by the example of the CO_2 molecule: the symmetric stretching vibration ν_1 (cf. Fig. 10.10) is infra-red inactive, since the centres of positive and negative charge in the molecule coincide during the vibration. This motion is, however, Raman-active, since the polarisability changes periodically as a result of the stretching vibration. The asymmetric stretching vibration ν_2 , in contrast, is infra-red active, since here, an electric dipole moment is present: however, it is Raman-inactive, because the changes in the polarisability due to the shortening and lengthening of the two C–O bonds in the molecule just compensate each other.

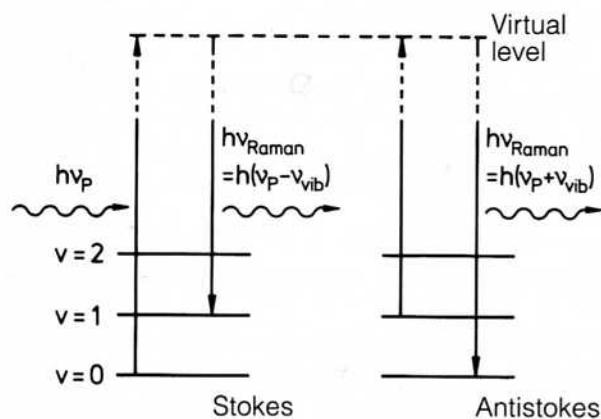
The classical theory of the Raman effect which we have described here explains many of the observations well, but it fails when the intensities are considered. In the classical picture, the same intensities would be expected for the lines which are shifted to lower energies and those shifted to higher energies, i.e. the Stokes and anti-Stokes lines. In fact, the Stokes lines are much more intense.

This is understandable in the light of the *quantum-mechanical* treatment of the Raman effect, which is given in Sect. 17.2. In this theory, the Raman Effect is treated as inelastic photon scattering, which in the case of the Stokes lines begins with a level having a small vibrational quantum number ν (in particular $\nu = 0$) and ends with a level having a higher quantum number ν' (for example $\nu' = 1$), while the reverse process occurs in the anti-Stokes effect: the scattering begins in an excited vibrational level and ends in a level with a smaller ν , e.g. in the ground state; see Fig. 12.3. So, for the Stokes lines without rotation, the wavenumber of the scattered light is given by:

$$\bar{\nu} = \bar{\nu}_p - \bar{\nu}_{\text{vib}} \quad (\text{or } 2\bar{\nu}_{\text{vib}} \text{ etc.}) \quad (12.6)$$

and for anti-Stokes lines:

Fig. 12.3. A schematic representation of vibrational Raman scattering, to illustrate the Stokes and anti-Stokes scattering. Primary light of wavenumber $\bar{\nu}_p$ connects a real excitation state of the molecule with a virtual state. The Raman-scattered light has lost energy (Stokes lines) or gained energy (anti-Stokes lines) relative to the primary light



$$\bar{\nu} = \bar{\nu}_p + \bar{\nu}_{\text{vib}} \text{ (or } 2\bar{\nu}_{\text{vib}} \text{ etc.) .}$$

The difference $\bar{\nu}_p - \bar{\nu}$ is called the Raman shift. As we already pointed out, $\bar{\nu}_p$ is the wavenumber of the primary light which excites the transition and $\bar{\nu}_{\text{vib}}$ is the wavenumber of the molecular vibration.

In the case of Stokes Raman scattering, the molecule takes on energy from the photon; in anti-Stokes scattering, it gives up energy to the photon. The intensity ratios between Stokes and anti-Stokes lines are thus given by the occupation probabilities n of the initial states, and these can be calculated from the Boltzmann factor in thermal equilibrium. They are, in any case, different for Stokes and anti-Stokes transitions. The intensity of the anti-Stokes lines of course must decrease with decreasing temperature, since this process presumes that the molecule is initially in an excited vibration state, and the number of such molecules decreases when the temperature is lowered.

For the intensities, we then find

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \frac{n(v=1)}{n(v=0)} = e^{-h\nu_{\text{vib}}/kT} \quad (12.7)$$

If we set $\nu_{\text{vib}} = 1000 \text{ cm}^{-1}$ and $T = 300 \text{ K}$ in this expression, we obtain a numerical value of e^{-5} , i.e. 0.7% for the relative intensity.

Quantum-mechanically, the selection rules are $\Delta v = \pm 1$ (and ± 2 , ± 3 , with much smaller probabilities, since here the nonlinear contributions to the polarisability are responsible for the transitions). This subject will be treated in more detail in Sect. 17.2.

12.3 Rotational Raman Spectra

Now we turn to the *rotational Raman effect* (Figs. 12.4, 5). Here, again, one observes a series of scattering lines on both sides of the Rayleigh (i.e. the primary) line, but now with spacings corresponding to the rotational quanta. Here, also, many aspects of the observed effect can be understood classically. The polarisability of a nonspherical molecule is, as we have already discussed in Sect. 3.2, anisotropic and must be treated as a tensor with the principal polarisabilities α_{\parallel} and α_{\perp} , where parallel and perpendicular refer to the long and

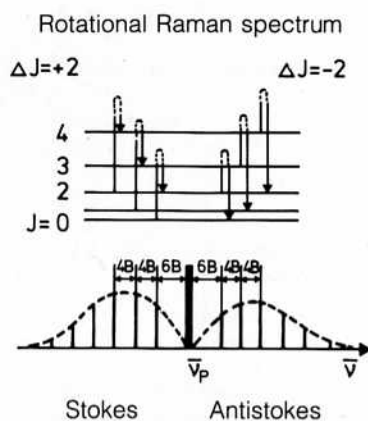
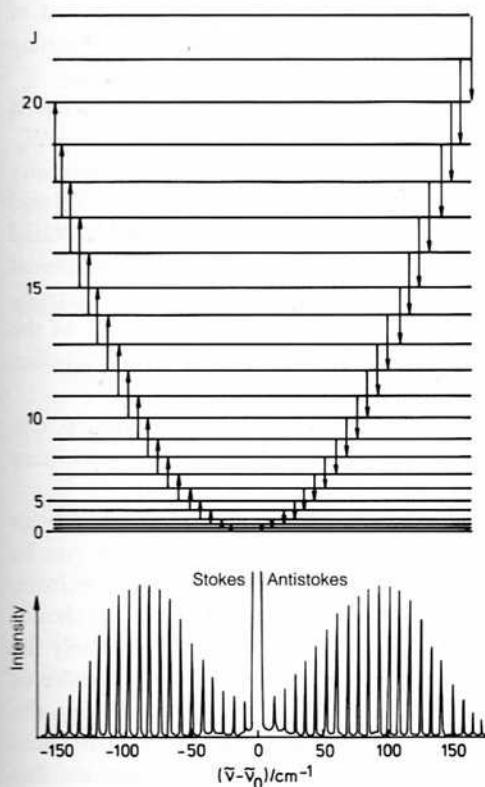


Fig. 12.4. A diagram explaining the occurrence of rotational Raman spectra. To the left and right of the Rayleigh line $\bar{\nu}_p$ are the Stokes and the anti-Stokes lines of the Raman spectrum

short axes of the polarisability tensor, i.e. usually the body axis and an axis perpendicular to it. The rotation of a molecule therefore also leads to a periodic modulation of the dipole moment induced by the E field of the primary light and thus to a modulation of the frequency of the scattered radiation. This frequency modulation, however, occurs at $2\nu_{\text{rot}}$, since the same polarisability as at the beginning of the rotation recurs after a rotation through 180° owing to the tensor symmetry. The additional lines accompanying the primary light thus occur at spacings corresponding to twice the rotational frequency.

This can be made clear by a simple demonstration experiment, which is shown in Fig. 12.6. The light from a lamp operated at a frequency of 50 Hz is reflected by two white balls in a dumbbell model which can rotate about an axis perpendicular to the line joining the balls and represents a linear dumbbell-molecule. The reflected light then contains, in addition to the unshifted component modulated at 50 Hz, two sidebands at the shifted frequencies ($50 \pm 2\nu_{\text{rot}}$). This could be demonstrated by a simple frequency meter.



◀ Fig. 12.5

Fig. 12.5. The complete rotational Raman spectrum of a diatomic molecule consists of many nearly equidistant lines with a spacing of $4B$. Term scheme and intensity distribution are explained in the text. The selection rule is $\Delta J = \pm 2$. The Raman shift $\bar{\nu} - \bar{\nu}_p$ is negative for Stokes lines and positive for anti-Stokes lines

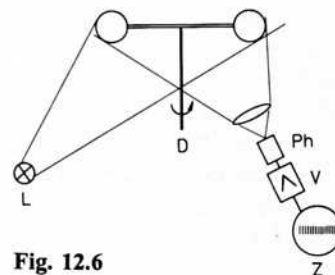


Fig. 12.6

Fig. 12.6. A demonstration experiment for the rotational Raman effect, after Auer. The light of a lamp L is reflected by two spheres which are rotating around the axis D . A frequency meter Z indicates the rotational frequency as an additional frequency to that of the modulation of the light (50 Hz). More details are given in the text

This classical model gives an explanation of the rotational Raman effect which is at least qualitatively satisfactory. It is determined by the difference $\alpha_{\parallel} - \alpha_{\perp}$, i.e. the anisotropy in the polarisability of the molecule, and occurs only when $\alpha_{\parallel} - \alpha_{\perp}$ is nonzero. This condition is fulfilled for all diatomic molecules, even for nonpolar molecules such as H_2 , N_2 , as well as for CO_2 . For symmetric tetrahedral molecules such as CH_4 or CCl_4 , in contrast, one finds $\alpha_{\parallel} = \alpha_{\perp}$, and there is thus no rotational Raman effect. The classical explanation for the occurrence of the *doubled* rotational frequency in the spacing of the Raman lines is

reproduced in quantum mechanics in terms of modified selection rules which correspond to a two-photon process.

The quantum-mechanical treatment of the rotational Raman effect as inelastic photon scattering accompanied by the uptake or release of rotational quanta leads to the selection rule $\Delta J = \pm 2$ in the case of the linear rotor. For the rigid rotor with energy levels $E_J = BJ(J+1)$, the shift of the rotational Raman lines relative to the primary light is given by

$$\bar{\nu}_{\text{rot}} = \pm B[(J+2)(J+3) - J(J+1)] = \pm B[4J+6] \quad (\text{cm}^{-1}), \quad (12.8)$$

where the sign is relative to the primary frequency of the exciting light.

For the wavenumber of the Raman-scattered light, we find

$$\bar{\nu} = \bar{\nu}_p \pm \bar{\nu}_{\text{rot}}.$$

In a transition with $\Delta J = +2$, the molecule is raised to a higher rotational state by the scattering process. The wavenumber of the scattered light is therefore smaller than that of the primary light, $\bar{\nu}_p$. The Stokes lines of the spectrum thus appear on the low-frequency side of the primary light. For the anti-Stokes lines, with $\Delta J = -2$, the reverse is true.

The rotational Raman spectrum of a linear molecule thus has the structure which is shown in Fig. 12.4. The first Raman line, with $J = 0$, is located at a distance $6B$ from $\bar{\nu}_p$, the primary line, and then the other lines follow at a constant spacing of $4B$. The intensity distribution in a rotational Raman spectrum is given, as in the rotational spectra treated earlier, by the thermal populations and the multiplicities of the J terms. It is demonstrated in Fig. 12.5. In addition, this figure makes clear that due to the smallness of the rotational quanta, the number of rotational lines in the spectrum may be quite large. The difference in thermal populations between neighbouring levels is, as a result of the smallness of the rotational quanta, very little in comparison to kT ; thus the difference in intensity between the Stokes and the anti-Stokes lines is also small.

The selection rules depend on the symmetry of the molecule. For the symmetric top, e.g. CH_3Cl , we have $\Delta J = 0, \pm 1, \pm 2$, and $\Delta K = 0$. Its rotational Raman spectrum has more lines than that of the linear rotor; we shall however not go into this further here.

We are now in a position to understand the *rotational structure in the vibrational Raman spectrum*. Each vibrational Raman line is accompanied by rotational lines, which can be understood in the same way as the rotational structure in a rotational-vibrational spectrum, but taking into account the different selection rules for Raman transitions. Figure 12.7 shows, as an example of a measured spectrum, a section of the Raman spectrum of $^{16}\text{O}_2$, namely the vibrational line at $\bar{\nu}_e = 1556 \text{ cm}^{-1}$, and its accompanying rotational lines. The structure of this Raman spectrum corresponds to that of the infra-red vibrational spectrum, but now the selection rules are $\Delta v = \pm 1 (\pm 2, \dots)$, $\Delta J = 0, \pm 2$. The comparison gives the differences between a rotational-vibrational spectrum and a rotational-vibrational Raman spectrum; this is illustrated schematically in Fig. 12.8.

Let us now compare the rotational-vibrational spectrum (without the Raman Effect) to the corresponding Raman spectrum, referring to Fig. 12.8.

In the *rotational-vibrational spectrum* of a diatomic molecule, for $\Delta v = 1$ there are

$$\text{the } R \text{ branch, } \bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}}, \quad \Delta J = 1, \quad \bar{\nu}_{\text{rot}} = 2B(J+1)$$

$$\text{the } P \text{ branch, } \bar{\nu}_{\text{vib}} - \bar{\nu}_{\text{rot}}, \quad \Delta J = -1, \quad \bar{\nu}_{\text{rot}} = 2B J$$

and possibly

$$\text{the } Q \text{ branch, } \bar{\nu}_{\text{vib}}, \quad \Delta J = 0.$$

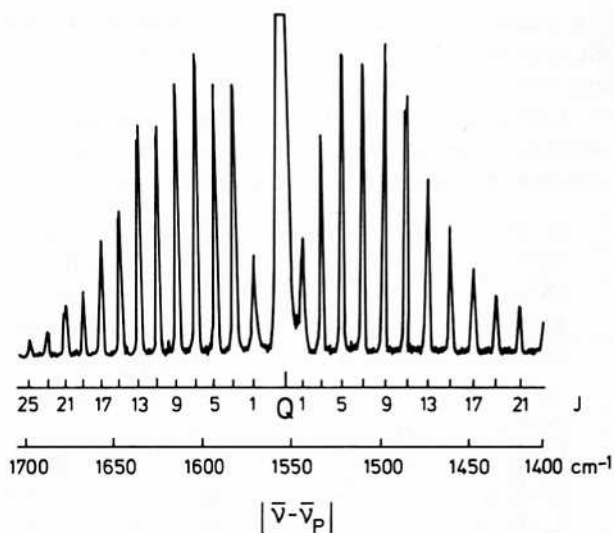


Fig. 12.7. A section of the rotational-vibrational Raman spectrum of oxygen, $^{16}\text{O}_2$. This is a vibrational line (Stokes line) with its accompanying rotational lines. In the centre, at the energy of the vibrational wavenumber $\bar{\nu}_e = 1556 \text{ cm}^{-1}$, we see the Q branch ($\Delta J = 0$) as a broad line. For $^{16}\text{O}_2$ ($I = 0$), the lines with even J are missing; cf. Sect. 12.4. After Hellwege

By contrast, in the *Raman spectrum*, for Stokes lines with $\Delta v = +1$, we have

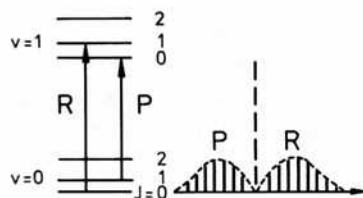
$$\begin{aligned} \text{the } S \text{ branch, } & \bar{\nu}_p - (\bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}}), & \Delta J = 2 \\ \text{the } Q \text{ branch, } & \bar{\nu}_p - \bar{\nu}_{\text{vib}}, & \Delta J = 0 \\ \text{the } O \text{ branch, } & \bar{\nu}_p - (\bar{\nu}_{\text{vib}} - \bar{\nu}_{\text{rot}}), & \Delta J = -2. \end{aligned} \quad (12.9)$$

Here, $\bar{\nu}_{\text{rot}}$ is an abbreviation for the rotational energy, $B(4J + 6)$; see (12.8).

Vibrational spectrum

$$\Delta J = +1 \text{ (R branch)} \quad \bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}}$$

$$\Delta J = -1 \text{ (P branch)} \quad \bar{\nu}_{\text{vib}} - \bar{\nu}_{\text{rot}}$$



Vibrational raman spectrum

$$\Delta J = 2 \text{ (S branch)} \quad \bar{\nu}_p - (\bar{\nu}_{\text{vib}} + \bar{\nu}_{\text{rot}})$$

$$\Delta J = 0 \text{ (Q branch)} \quad \bar{\nu}_p - \bar{\nu}_{\text{vib}}$$

$$\Delta J = -2 \text{ (O branch)} \quad \bar{\nu}_p - (\bar{\nu}_{\text{vib}} - \bar{\nu}_{\text{rot}})$$

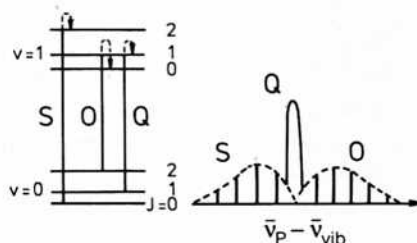


Fig. 12.8. A vibrational Raman spectrum (*right*) compared to a rotational-vibrational spectrum (*left*), schematically. Only a section of each spectrum is shown. The selection rules and therefore the rotational structure of the two spectra are different. Here, we show only Stokes lines in the Raman spectrum, i.e. lines having a lower frequency than that of the primary light. The Raman shift is $\bar{\nu}_p - \bar{\nu}_{\text{vib}}$, where $\bar{\nu}_p$ refers to the primary light and $\bar{\nu}_{\text{vib}}$ to a vibrational wavenumber

The anharmonicity and the coupling have been left out of these considerations; cf. Chap. 9. Both effects lead to small shifts in the spectra, as we have already seen in Sects. 9.2.3 and 9.5; these can usually not be determined so accurately in the Raman spectrum. For large molecules, the rotational fine structure of the Raman spectrum is barely resolvable.

The whole Raman spectrum of a molecule was already indicated schematically in Fig. 12.1, and now becomes clear. Immediately adjacent to the Rayleigh line, the line from the primary light, we see the rotational lines. At a spacing corresponding to the vibrational line,

$\bar{\nu}_{\text{vib}}$, one observes the Stokes region of the rotational-vibrational lines, and with reduced intensity on the other side, the anti-Stokes lines. This structure repeats with decreasing intensity as “harmonics” in the range $\pm 2\bar{\nu}_{\text{vib}}$.

Raman spectroscopy is thus a second method for measuring molecular rotational and vibrational quanta. What, then, are its advantages, or at least the differences, relative to infra-red or microwave spectroscopies?

- By properly choosing the primary light, one can shift the investigation of rotational and vibrational spectra from the microwave and infra-red spectral ranges to *more conveniently accessible spectral regions*, namely into the range of visible light.
- There are vibrations and rotations of molecules which are visible in the Raman spectrum, but not in the infra-red or microwave spectra. For example, diatomic homonuclear molecules such as H_2 , N_2 , or O_2 can be investigated *only with Raman spectroscopy*, since their rotations and vibrations are infra-red inactive.
- From the polarisation behaviour of Raman spectra, one can obtain information about the *polarisability tensor* of the molecules. A depolarisation of the Raman spectrum as compared to the primary light allows the motions of the molecules in the surrounding medium during the scattering process, particularly in liquids, to be studied; the molecules change not only their positions, but also their orientations in the course of these motions. When the molecule moves during the scattering process, the polarisation diagram for the scattered radiation can deviate from that calculated for a motionless molecule.
- In the Raman effect, in contrast to the usual single-photon spectroscopies, the *parity* of the state is conserved. The reason for this is the fact that two photons take part in the overall process. In single-photon dipole processes, the parity changes; in two photon processes, it changes twice, i.e. it returns to its initial value.
- The intensity of the Raman effect is largely independent of the frequency of the primary light, as long as the quantum energy of the light is sufficiently far removed from that of an electronic transition. The light quantum of excitation of the Raman effect, $h\nu_p$, ends in a so-called virtual level; cf. Fig. 12.3. If the quantum energy of the primary light approaches that of an electronic transition, i.e. a real excitation level, then the Raman scattering intensity increases. This amplification of the Raman spectrum is called the *resonant Raman effect*.

Using the resonant Raman effect, particular parts of large, complex molecules can be investigated specifically, by intentionally using primary light whose frequency is near to that of a real excitation in the molecular subgroup. In that case, the portion of the Raman spectrum originating from the particular subgroup and containing its rotational and vibrational structure is strongly enhanced relative to the Raman spectra of other molecular subgroups.

12.4 The Influence of Nuclear Spins on the Rotational Structure

In the rotational spectrum and in the rotational-vibrational spectrum of homonuclear diatomic molecules such as H_2 , N_2 , and O_2 , and quite generally in the spectra of molecules with a centre of inversion symmetry, such as CO_2 , characteristic intensity differences are observed in the lines originating from levels with an even rotational quantum number J as compared to those originating from levels with an odd value of J . Examples are shown in Figs. 12.7

and 12.11. Since such spectra are often (but not exclusively – see for example the rotational-vibrational spectrum of CO_2 in Fig. 10.12) investigated as Raman spectra, we will consider this interesting and important aspect of molecular spectra at this point. The effect is due to the influence of the *nuclear spins* on the spectra.

The nuclear spins and the magnetic moments of the nuclei of course interact with the electronic shell of a molecule, but the influence of this interaction on the electronic spectra is comparatively small. The resulting hyperfine structure of the molecular terms and the spectral lines is based on the same interaction mechanism as in atoms. It can be investigated by using high-resolution spectroscopy, but we will not deal with this here; the subject is treated in more detail in I, Chap. 20.

The observed intensity variations in the Raman spectra are due, however, to a different phenomenon of fundamental importance: the influence of the nuclear spins on the *statistics*, that is the relative probability with which particular molecular states occur. In molecules with two identical nuclei, the observed intensity distribution in the spectrum is a result of the influence of the nuclear spins on the symmetry of the overall wavefunction of the molecular state. It is due to the Pauli exclusion principle, according to which the overall wavefunction of fermions, i.e. particles with half-integral spins, must be antisymmetric with respect to exchange of the particles. In the case of bosons, with integral spins, the wavefunction must be symmetric under particle exchange. Here, we are dealing with nuclear fermions (e.g. ^1H , with $I = 1/2$) and nuclear bosons (e.g. ^{16}O , with $I = 0$).

Let us consider the H_2 molecule in order to explain this effect; see Fig. 12.9. The two protons in the molecule are fermions with spin $1/2$. The spins of the two protons may be parallel; then the molecule has a total nuclear spin quantum number of $I = 1$. The spin wavefunction is symmetric with respect to particle exchange, as the particles are indeed identical when their spins are parallel. This kind of hydrogen is called ortho hydrogen, $o\text{-H}_2$. The two nuclear spins could, however, also be antiparallel, and the total spin quantum number would then be 0. In this case, the spin wavefunction is antisymmetric with respect to

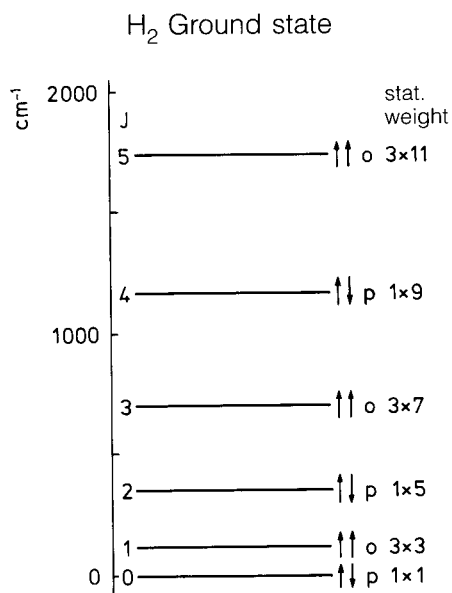


Fig. 12.9. The rotational levels of the H_2 molecule in the ground state, with the spin orientations of the nuclei (ortho and para- H_2) and the statistical weights of the configurations. Ortho hydrogen has rotational levels with odd values of J , while para hydrogen has levels of even J .

exchange of the nuclei, and this configuration is termed para hydrogen, p-H₂. The statistical weight of the two configurations is 3:1, as shown in Table 12.1.

Table 12.1. o- and p-hydrogen

	I	M_I	Wavefunction	Character
o-H ₂	1	1	$\uparrow\uparrow$	triplet
		0	$\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$	
		-1	$\downarrow\downarrow$	
p-H ₂	0	0	$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$	singlet

The overall wavefunction of the molecule is the product of the spatial functions (including rotation) and the spin functions. Exchange of the nuclei means in the case of a dumbbell molecule simply a reversal of the dumbbell, equivalent to an inversion in space. Under this operation, the rotational eigenfunctions for $J = 1, 3, 5, \dots$ change their signs (cf. Sect. 11.1); they have negative parity and are antisymmetric with respect to exchange. The rotational functions with $J = 0, 2, 4, \dots$ remain unchanged; they have positive parity and are symmetric.

The overall parity is the product of the parities of the functions contributing to the total system. For particles with half-integral spin, it must be negative. Then o-H₂, i.e. hydrogen molecules with $I = 1$ and thus positive parity of the spin function, must have rotational states with negative parity, i.e. $J = 1, 3, 5, \dots$ with the statistical weight 3, if the remaining spatial function has positive parity, as is in fact the case for the ground state of hydrogen. As we shall see in Sects. 13.3 and 13.4, this is true of the state denoted by $^1\Sigma_g^+$, the ground state of the hydrogen molecule. Para hydrogen, with $I = 0$ and negative parity of the spin function, must have rotational functions with $J = 0, 2, 4, \dots$, so that the overall product gives a negative parity for the total wavefunction.

Between these two types of hydrogen, which by the way can be separated from each other macroscopically, transitions are rather strictly forbidden. Only transitions within the term system with even J and within that with odd J are possible, if the nuclei are completely uncoupled. The weak coupling between the nuclear spins and the electronic shells does, however, make transitions between the two systems possible, with a very small transition probability.

At the lowest temperatures, only p-H₂ is stable; o-H₂, due to its $J = 1$, i.e. because a rotational quantum is excited, is metastable. The spontaneous conversion of o-H₂ into p-H₂ by flipping of a nuclear spin occurs very slowly, over a time of years. This process can be accelerated by addition of paramagnetic materials or other catalysts, so that pure p-H₂ can be prepared at low temperatures. It remains in the p-H₂ state for some time even after warming and evaporation to H₂ gas. The case of deuterium or heavy hydrogen, ²H₂ or D₂, is just the reverse: the nuclear spin of ²H is $I = 1$, the nucleus is a boson, and at low temperatures, ortho-D₂ is stable and para-D₂ is metastable.

Normally, thermal equilibrium is established between the two H₂ modifications. Hydrogen is a mixture of p-H₂ and o-H₂ in the ratio 1:3. This has the following consequences for the rotational spectrum (see Fig. 12.10):

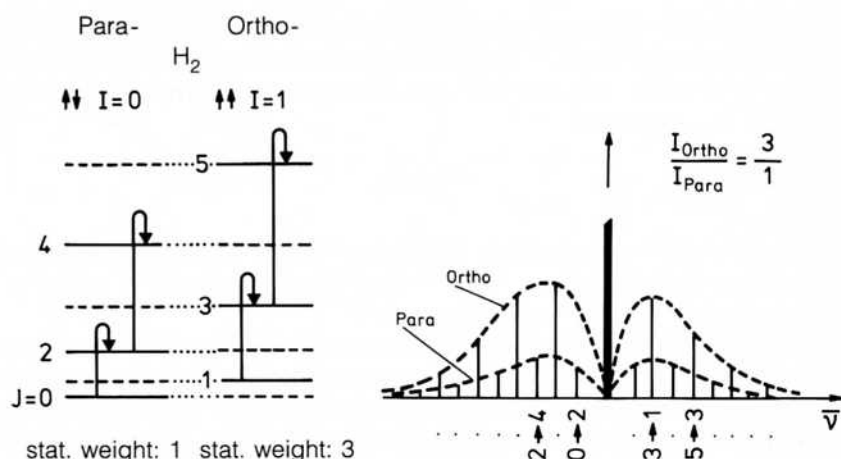


Fig. 12.10. The rotational Raman spectrum of the H_2 molecule. The overall spectrum is a superposition of the spectra of ortho and para hydrogen, with the intensity ratio 3:1. The direct line at the centre of the spectrum is the Rayleigh line

- In the rotational spectrum, there can be no transitions with $\Delta J = \pm 1$, and therefore no allowed transitions at all. They would in any case be infra-red inactive due to the lack of a dipole moment in H_2 .
- Rotational Raman lines with $\Delta J = \pm 2$ are, in contrast, allowed. They belong alternately to o- and p- H_2 . For this reason, alternating intensities are observed in the Raman spectrum, as can be seen in Fig. 12.10.

The observed alternating intensities in the spectra of other homonuclear molecules can be understood in an analogous manner. For $^{16}O_2$, with $I = 0$, all the levels with even J quantum number are lacking, for example. Here, the electronic wavefunction in the ground state has negative parity (term symbol $^3\Sigma_g^-$). In order to make the overall wavefunction symmetric (^{16}O is a boson) with respect to exchange, the rotational wavefunctions must also have negative parity. Thus, the rotational lines with even J are missing in the spectrum; compare Fig. 12.7. For ^{14}N , with $I = 1$, all the lines in the Raman rotational branches are observed in the spectrum of the N_2 molecule, but with alternating intensities in the ratio 1:2, which results from the possible spin configurations in the molecule. These are parallel, with $I_{\text{tot}} = 2$, and antiparallel, with $I_{\text{tot}} = 0$; see Fig. 12.11. For N_2 molecules with two different isotopes, i.e. $^{14}N^{15}N$, this alternating intensity is lacking in the Raman spectrum.

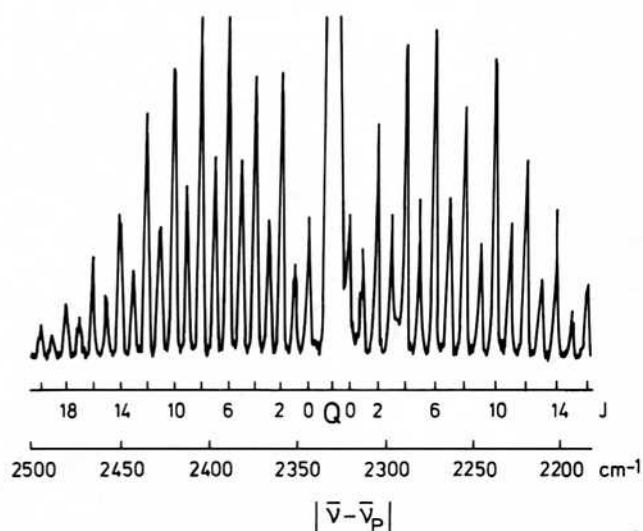


Fig. 12.11. The rotational-vibrational Raman spectrum of the nitrogen molecule, $^{14}N_2$. In the centre, at the position of the vibrational wavenumber $\bar{\nu}_e = 2330 \text{ cm}^{-1}$, the Q branch ($\Delta J = 0$) appears as a broad line. In $^{14}N_2$, with $I = 1$, an alternating intensity of the rotational lines with a ratio 1:2 is observed. After Hellwege

In general, the following rules hold, which we give here without a detailed derivation:

The ratio of the statistical weights of antisymmetric and symmetric states of the nuclear spins in a diatomic molecule with two identical nuclei having the nuclear spin quantum number I is

$$\frac{g_a}{g_s} = \frac{I}{I+1} \quad (12.10)$$

This is then also the intensity ratio of alternate lines in the rotational spectrum; for H_2 , with $I = 1/2$, we find 3:1, for N_2 , with $I = 1$, we find 2:1, and for O_2 , with $I = 0$, one of the two components is completely lacking, i.e. 1:0.

The molecule C^{16}O_2 is particularly illustrative; it is linear and therefore has a centre of inversion symmetry. Here, only rotational levels with an even quantum number J are allowed, since the electronic ground state has positive parity ($^1\Sigma_g^+$). We pointed this fact out already with respect to the rotational-vibrational spectrum of the CO_2 molecule, shown in Fig. 10.12, without being able to explain it at that point. On the other hand, if one investigates molecules having two different oxygen isotopes, e.g. $^{16}\text{O}^{18}\text{O}$, then the symmetry is lowered, since the two O nuclei are now different. For this molecule, *all* the rotational terms are observed in the spectrum, which thus contains twice as many lines.

The influence of the nuclear spins on the statistics of the possible molecular states which we have described cannot be explained within classical physics and presents an impressive demonstration of the correctness of quantum-mechanical concepts, in particular the Pauli principle. Simply observing the intensity pattern in the rotational spectrum of a molecule permits the determination of the nuclear spin quantum number I from (12.10).