

**Figure 11B.12** The rotational energy levels of a linear rotor and the transitions allowed by the  $\Delta J = \pm 2$  Raman selection rules. The form of a typical rotational Raman spectrum is also shown. In practice the Rayleigh line is much stronger than depicted in the figure.

For anti-Stokes lines  $\Delta J = -2$  and the scattered radiation is at a higher wavenumber, the shift being the difference  $\tilde{F}(J) - \tilde{F}(J-2)$ :

$$\begin{aligned}\tilde{\nu}(J-2 \leftarrow J) &= \tilde{\nu}_i + \{\tilde{F}(J) - \tilde{F}(J-2)\} \\ &= \tilde{\nu}_i + 2\tilde{B}(2J-1)\end{aligned}\quad \begin{array}{l} \text{Wavenumbers} \\ \text{of anti-Stokes} \\ \text{lines: linear rotor} \end{array} \quad (11B.24b)$$

The Stokes lines appear to low frequency of the incident radiation and at displacements  $6\tilde{B}$ ,  $10\tilde{B}$ ,  $14\tilde{B}$ , ... from  $\tilde{\nu}_i$  for  $J = 0, 1, 2, \dots$ . The anti-Stokes lines occur at displacements of  $6\tilde{B}$ ,  $10\tilde{B}$ ,  $14\tilde{B}$ , ... (for  $J = 2, 3, 4, \dots$ ;  $J = 2$  is the lowest state that can contribute under the selection rule  $\Delta J = -2$ ) to high frequency of the incident radiation. The separation of adjacent lines in both the Stokes and the anti-Stokes regions is  $4\tilde{B}$ , so from the spacing  $I_{\perp}$  can be determined and then used to find the bond length exactly as in the case of microwave spectroscopy.

#### Example 11B.4 Predicting the form of a Raman spectrum

Predict the form of the rotational Raman spectrum of  $^{14}\text{N}_2$ , for which  $\tilde{B} = 1.99 \text{ cm}^{-1}$ , when it is exposed to  $336.732 \text{ nm}$  laser radiation.

**Collect your thoughts** The molecule is rotationally Raman active because end-over-end rotation modulates its polarizability as viewed by a stationary observer. The wavenumbers of the Stokes and anti-Stokes lines are given by eqn 11B.24.

**The solution** The incident radiation with wavelength  $336.732 \text{ nm}$  corresponds to a wavenumber of  $\tilde{\nu}_i = 29697.2 \text{ cm}^{-1}$ ; eqns 11B.24a and 11B.24b give the following line positions:

$J$	0	1	2	3
Stokes lines				
$\tilde{\nu}/\text{cm}^{-1}$	29685.3	29677.3	29669.3	29661.4
$\lambda/\text{nm}$	336.867	336.958	337.048	337.139

$J$	0	1	2	3
Anti-Stokes lines				
$\tilde{\nu}/\text{cm}^{-1}$			29709.1	29717.1
$\lambda/\text{nm}$			336.597	336.507

There will be a strong central line at  $336.732 \text{ nm}$  accompanied on either side by lines of increasing and then decreasing intensity (as a result of transition moment and population effects). The spread of the entire spectrum is very small, so the incident light must be highly monochromatic.

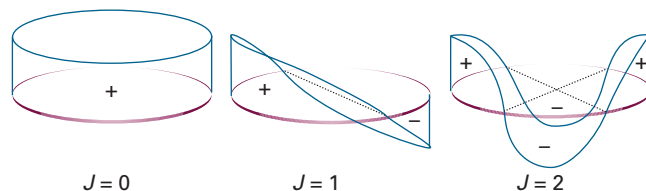
**Self-test 11B.4** Repeat the calculation for the rotational Raman spectrum of  $^{35}\text{Cl}_2$  ( $\tilde{B} = 0.9752 \text{ cm}^{-1}$ ).

*Answer:* Stokes lines at  $29691.3, 29687.4, 29683.5, 29679.6 \text{ cm}^{-1}$ , anti-Stokes lines at  $29703.1, 29707.0 \text{ cm}^{-1}$ .

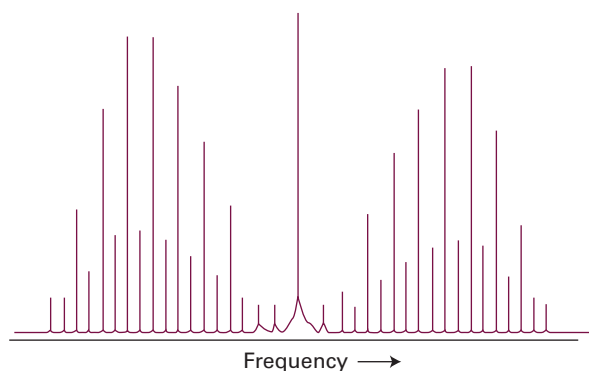
## 11B.4 Nuclear statistics and rotational states

If eqn 11B.24 is used to analyse the rotational Raman spectrum of  $\text{C}^{16}\text{O}_2$ , the rotational constant derived from the spacing of the lines is inconsistent with other measurements of C–O bond lengths. The results are consistent if it is supposed that the molecule can exist in states with only even values of  $J$ , so the observed Stokes lines are  $2 \leftarrow 0, 4 \leftarrow 2, \dots$ ; the lines  $3 \leftarrow 1, 5 \leftarrow 3, \dots$  are missing.

The explanation of the missing lines lies in the Pauli principle (Topic 8B) and the fact that  $^{16}\text{O}$  nuclei are spin-0 bosons: just as the Pauli principle excludes certain electronic states, so too does it exclude certain molecular rotational states. The Pauli principle states that, when two identical bosons are exchanged, the overall wavefunction must remain unchanged. When a  $\text{C}^{16}\text{O}_2$  molecule rotates through  $180^\circ$ , two identical  $^{16}\text{O}$  nuclei are interchanged, so the overall wavefunction of the molecule must remain unchanged. However, inspection of the form of the rotational wavefunctions (which have the same angular dependence as the s, p, etc. orbitals of atoms) shows that they change sign by  $(-1)^J$  under such a rotation (Fig. 11B.13). Therefore, only even values of  $J$  are permissible for  $\text{C}^{16}\text{O}_2$ , and hence the Raman spectrum shows only alternate lines.



**Figure 11B.13** The symmetries of rotational wavefunctions (shown here, for simplicity as a two-dimensional rotor) under a rotation through  $180^\circ$  depend on the value of  $J$ . Wavefunctions with  $J$  even do not change sign; those with  $J$  odd do change sign.



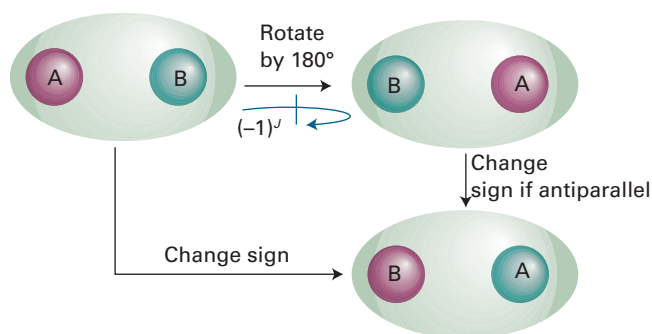
**Figure 11B.14** The rotational Raman spectrum of a homonuclear diatomic molecule with two identical spin- $\frac{1}{2}$  nuclei shows an alternation in intensity as a result of nuclear statistics. In practice the Rayleigh line is much stronger than depicted in the figure.

The selective existence of rotational states that stems from the Pauli principle is termed **nuclear statistics**. Nuclear statistics must be taken into account whenever a rotation interchanges equivalent nuclei. However, the consequences are not always as simple as for  $\text{C}^{16}\text{O}_2$  because there are complicating features when the nuclei have non-zero spin: it is found that there are several different relative nuclear spin orientations consistent with even values of  $J$  and a different number of spin orientations consistent with odd values of  $J$ . For  $^1\text{H}_2$  and  $^{19}\text{F}_2$ , which have two identical spin- $\frac{1}{2}$  nuclei, by using the Pauli principle it can be shown that there are three times as many ways of achieving a state with odd  $J$  than with even  $J$ , and there is a corresponding 3:1 alternation in intensity in their rotational Raman spectra (Fig. 11B.14).

#### How is that done? 11B.2 Identifying the effect of nuclear statistics

Because  $^1\text{H}$  nuclei have  $I = \frac{1}{2}$ , like electrons, they are fermions and the Pauli principle requires the overall wavefunction to change sign under particle interchange. However, the rotation of a  $^1\text{H}_2$  molecule through  $180^\circ$  has a more complicated effect than simply relabelling the nuclei (Fig. 11B.15).

There are four nuclear spin wavefunctions: three correspond to a total nuclear spin  $I_{\text{total}} = 1$  (parallel spins,  $\uparrow\uparrow$ ); and one with  $I_{\text{total}} = 0$  (paired spins,  $\uparrow\downarrow$ ). The three wavefunctions with  $I_{\text{total}} = 1$  are  $\alpha(A)\alpha(B)$ ,  $\alpha(A)\beta(B) + \alpha(B)\beta(A)$ , and  $\beta(A)\beta(B)$  with  $M_I = +1, 0$ , and  $-1$ , respectively. Rotation of the molecule through  $180^\circ$  interchanges the labels A and B, but overall these three wavefunctions are unchanged. Therefore, to achieve an overall change of sign, the rotational wavefunction must change sign, and so only odd values of  $J$  are allowed.



**Figure 11B.15** The interchange of two identical fermion nuclei results in the change in sign of the overall wavefunction. The relabelling can be thought of as occurring in two steps: the first is a rotation of the molecule; the second is the interchange of unlike spins (represented by the different colours of the nuclei). The wavefunction changes sign in the second step if the nuclei have antiparallel spins.

The fourth wavefunction, with  $I_{\text{total}} = 0$  and  $M_I = 0$ , is  $\alpha(A)\beta(B) - \alpha(B)\beta(A)$ . When the labels A and B are interchanged the nuclear spin wavefunction changes sign:  $\alpha(A)\beta(B) - \alpha(B)\beta(A) \rightarrow \alpha(B)\beta(A) - \alpha(A)\beta(B) \equiv -\{\alpha(A)\beta(B) - \alpha(B)\beta(A)\}$ . Therefore, in this case for the overall wavefunction to change sign requires that the rotational wavefunction not change sign. Hence, only even values of  $J$  are allowed.

The analysis leads to the conclusion that there are three nuclear spin wavefunctions that can be combined with odd values of  $J$ , and one wavefunction that can be combined with even values of  $J$ . In accord with the prediction of eqn 11B.25, the ratio of the number of ways of achieving odd  $J$  to even  $J$  is 3:1. In general, for a homonuclear diatomic molecule with nuclei of spin  $I$ , the numbers of ways of achieving states of odd and even  $J$  are in the ratio

$$\frac{\text{Number of ways of achieving odd } J}{\text{Number of ways of achieving even } J} = \begin{cases} (I+1)/I & \text{for half-integral spin nuclei} \\ I/(I+1) & \text{for integral spin nuclei} \end{cases}$$

Nuclear statistics: homonuclear diatomics (11B.25)

For  $^1\text{H}_2$ ,  $I = \frac{1}{2}$  and the ratio is 3:1. For  $^{14}\text{N}_2$ , with  $I = 1$  the ratio is 1:2. Additional complications arise when the electronic state of the molecule is not totally symmetric (as for  $\text{O}_2$ , Topic 11F).

Nuclear statistics have consequences outside spectroscopy. Different relative nuclear spin orientations change into one another only very slowly, so a  $^1\text{H}_2$  molecule with parallel nuclear spins remains distinct from one with paired nuclear spins for long periods. The form with parallel nuclear spins is called **ortho-hydrogen** and the form with paired nuclear spins is called **para-hydrogen**. Because *ortho*-hydrogen cannot exist in a state with  $J = 0$ , it continues to rotate at very low temperatures and has an effective rotational zero-point energy.