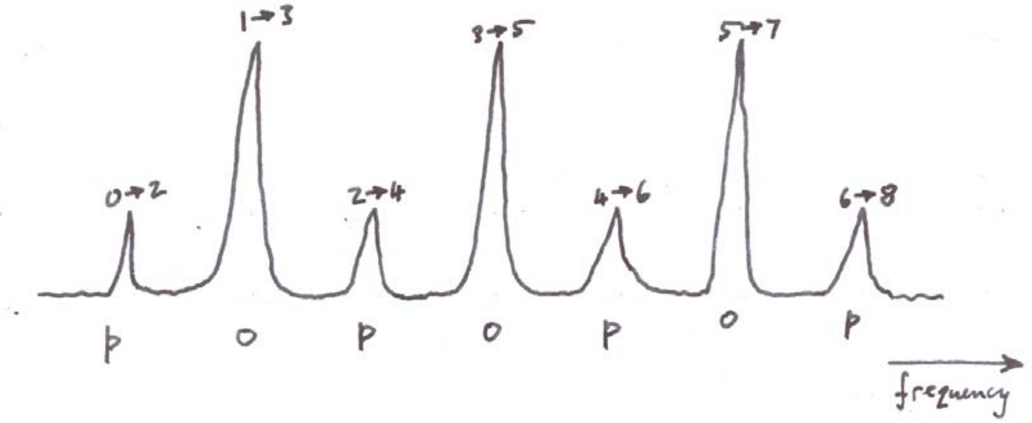
Spin-rotation isomerism

The influence of nuclear spin on the rotation of a diatomic molecule



Senior Sophister Hilary Term 2012

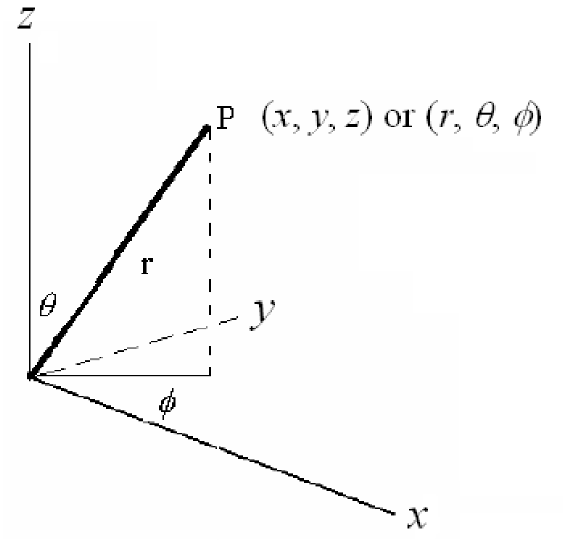
D.A.Morton-Blake

Spin isomerism

We shall consider the rotation of a *homonuclear linear molecule*, which includes not only homonuclear diatomic molecules like Cl_2 etc. but all those with a centre of symmetry such as O=C=O and H−C≡C−H.

The rigid rotor

If internal motions (vibrations) are neglected[1], the rotation of a rod-like object (linear molecule) of length r can be monitored by means of the two angles θ and φ. These are respectively the angles made by the object's *axis* with the z direction and by the xy-projection of the axis with the x direction. The quantities r, θ and φ constitute the spherical coordinates with which we are familiar. The figure identifies θ and φ as being equivalent to angles of longitude[2] and latitude respectively.



Transformation
cartesian to spherical

$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$

The system is equivalent to a pseudo-particle of mass μ moving in a field-free environment (zero potential energy). In the Schrödinger equation $H\psi = E\psi$ the Hamiltonian H for the system is

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \qquad (1)$$

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[1] We don't say that vibrations of the atoms are supposed not to occur, only that they are so fast (ν ≈ 10^{14} Hz) compared with the molecule's rotation (ν ≈ 10^{10} Hz) that the atoms can be taken as fixed at their mean positions during the molecule's rotational time period.

[2] The only difference is that geographical longitude is measured from the equator (the xy plane) whereas here θ is measured from the z axis.

and the eigenfunction ψ is a function of the two angular variables: $\psi \equiv \psi(\theta, \varphi)$. (It does not depend on r as this is fixed) Here μ is the mass of the pseudo-particle (effective mass of the molecule) and r is its distance from the origin (molecular length). The Hamiltonian is the result of using the three equations alongside the figure to transform the Laplacian operator $\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ from cartesian to spherical coordinates.

Since the variables are just the angles θ and φ, our system is in a two-dimensional space. The solutions to this equation are known from the 19th century when they were used to describe the vibrations of spheres. Before presenting them, just notice what happens to the Hamiltonian in eq. (1) if θ is constant at 90°. The first term vanishes leaving $H = -\frac{\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial \varphi^2}$. But this is the Hamiltonian for the rotation of a particle on a circle, a one dimensional problem, whose Schrödinger equation

$$H\psi_m = E_m\, \psi_m$$

we solved in the SF course to give

$$\psi_m = \sqrt{\frac{1}{2\pi}}e^{im\varphi} \qquad \text{and} \qquad E_m = \frac{m^2\hbar^2}{2\mu r^2}$$

We showed that the quantum number m takes values 0, ±1, ±2, ±3, …, defining quantized rotational energy levels.

Now here are the solutions to the two-dimensional problem defined by eq. (1). With a slight change of notation to customary ones for rotational systems the Schrödinger equation is

$$H\, Y_{J,M_J}(\theta,\varphi) = E_J\, Y_{J,M_J}(\theta,\varphi) \qquad (2)$$

Since we are not going to solve the equation we have anticipated some of the results in the way chosen to write eqn. (2)

1. The solutions are a set of mathematical functions called *spherical harmonics* $Y_{J,M_J}(\theta,\varphi)$.
2. These depend on a pair of quantum numbers J and M_J where J = 0, 1, 2, 3, … and M_J = 0, ±1, ±2, ±3, …
3. The energy eigenvalues, which are now given as

$$E_J = \frac{\hbar^2}{2I} J(J+1) \tag{3}$$

depend only on J (not M_J), so they are each $(2J+1)$-fold degenerate. Eqn. (3), in which the factor $2\mu r^2$ has been replaced by the moment of inertia I is the familiar one used to describe the rotational levels of a linear molecule.

$J = 3$ ————	7-fold degenerate ($M_J = 3, 2, 1, 0, -1, -2, -3$)
$J = 2$ ————	5-fold degenerate ($M_J = 2, 1, 0, -1, -2$)
$J = 1$ ————	3-fold degenerate ($M_J = 1, 0, -1$)
$J = 0$ ————	non-degenerate

Here are some of the rotational wave functions Y_{J,M_J}. Their normalization factors have been omitted for simplicity.

$$Y_{0,0} = 1$$

$$\begin{array}{llll}
Y_{1,+1} = \sin\theta\, e^{+i\varphi} & Y_{1,+1} + Y_{1,-1} = \sin\theta\,(e^{+i\varphi} + e^{-i\varphi}) & = 2\sin\theta\cos\varphi & \propto x \\
Y_{1,0} = \cos\theta & Y_{1,0} = & = \cos\theta & \propto z \\
Y_{1,-1} = \sin\theta\, e^{-i\varphi} & Y_{1,+1} - Y_{1,-1} = \sin\theta\,(e^{+i\varphi} + e^{-i\varphi}) & = 2i\sin\theta\sin\varphi & \propto y
\end{array}$$

$$\begin{array}{ll}
Y_{2,0} = 3\cos^2\theta - 1 & \propto 3z^2 - r^2 \\
Y_{2,\pm1} = \cos\theta\sin\theta\, e^{\pm i\varphi} & \propto xz, yz \\
Y_{2,\pm2} = \sin^2\theta\, e^{\pm 2i\varphi} & \propto x^2 - y^2, xy
\end{array}$$

They are spaced according to their J values, showing the 1, 3, 5, … degeneracies within the $J = 0, 1, 2, \ldots$ groups. Again notice that if the rotation were confined to a plane ($\theta = 90°$) the functions reduce to the solutions $e^{im\varphi}$ for a particle on a circle.

Symmetry properties

Consider the result on the rotational functions of subjecting them to the operation **i**, which entails inverting the molecule through its centre. This means carrying out the transformation $(x, y, z) \rightarrow (-x, -y, -z)$. In spherical coordinates that means $(\theta, \varphi) \rightarrow (\pi-\theta, \pi+\varphi)$. Conduct the transformation **i** on $Y_{1,-1}$ as an example:

$$\mathbf{i}\ Y_{1,-1} = \mathbf{i} \sin\,\theta\, \mathrm{e}^{-i\varphi} = \sin(\pi-\theta)\ \mathrm{e}^{-\mathrm{i}(\varphi+\pi)} = \sin\,\theta\,\mathrm{e}^{-i\varphi}\,\mathrm{e}^{-\mathrm{i}\pi} = Y_{1,-1}\ (-1) = -Y_{1,-1}$$

The behaviour of $Y_{1,-1}$ to inversion shows that it is an *odd* function. Performing this for each of the Y_{J,M_J} functions gives the results

$\mathbf{i}\ Y_{0,0} = Y_{0,0}$

$\mathbf{i}\ Y_{1,0} = -Y_{1,0}$ $\quad\mathbf{i}\ Y_{1,\pm1} = -Y_{1,\pm1}$

$\mathbf{i}\ Y_{2,0} = Y_{2,0}$ $\quad\mathbf{i}\ Y_{2,\pm1} = Y_{2,\pm1}$ $\quad\mathbf{i}\ Y_{2,\pm2} = Y_{2,\pm2}$

$\mathbf{i}\ Y_{3,0} = -Y_{3,0}$ $\quad\mathbf{i}\ Y_{3,\pm1} = -Y_{3,\pm1}$ $\quad\mathbf{i}\ Y_{3,\pm2} = -Y_{3,\pm2}$ $\quad\mathbf{i}\ Y_{3,\pm3} = -Y_{3,\pm3}$

The *parities* of the rotational wave functions (their symmetries with respect to inversion) alternate *odd* and *even* with successive *J*. That means that the energy levels correspond to *even* rotational states for even *J* and to *odd* states for odd *J*.

We shall see the significance of this remark about the parities of the rotational states presently, but it does provide an explanation of one of the selection rules for transitions between the rotational states. Recall that a transition is allowed between ψ_i and ψ_{i+1} but forbidden between ψ_i and ψ_{i+2}. The parities of the states shows why this is so. The ψ_i / ψ_{i+1} pair have different parities and so, because '*x*' has odd parity, the integrand in the transition moment integral $M^x_{i,i+1} \equiv \int \psi_i\ x\ \psi_{i+1}\, d\tau$ is even and $M^x_{i,i+1}$ is non-zero. In contrast, the ψ_i / ψ_{i+2} pair have equal parities and so the integrand is even and $M^x_{i,i+1}$ is zero.

The parity characteristics of rotational states, as developed above, will be used to answer this question "**If I were to interchange the positions of equivalent atoms in a molecule what effect would it have on the wave function?**"

Total wave function

A molecule or other assembly of particles may exhibit several types of motion. As well as *rotating* it might also be *vibrating* and its *electrons* would show a rich variety of quantized behaviour. As well as the wave functions describing these motions the quantum behaviour of nuclear spin may also be of importance in Chemistry. If you can think of any others, they can be included too, but the ones mentioned are those which will be relevant to the treatment that is to follow. Whether or not the component functions are independent of each other we can define a total wave function Ψ_{total} as

$$\Psi_{\text{total}} = \psi_{\text{rot}} \times \psi_{\text{vib}} \times \psi_{\text{el}} \times \psi_{\text{ns}} \qquad (4)$$

Fermions and bosons

Of the various schemes used to classify particles according to some set of properties we consider what happens when you interchange *two identical particles* in an assembly of particles.

1. The total wave function of the assembly changes sign. Mathematically this can be expressed as

   $$\Psi(1, 2, 3, \mathbf{4}, \mathbf{5}, 6, \ldots) = -\Psi(1, 2, 3, \mathbf{5}, \mathbf{4}, 6, \ldots)$$

   where the 5th and 6th identical particle has been interchanged. Particle systems showing this behaviour obey Fermi-Dirac ststistics and are called **fermions**.

2. The total wave function is unchanged by the switching of the particles, so

   $$\Psi(1, 2, 3, \mathbf{4}, \mathbf{5}, 6, \ldots) = \Psi(1, 2, 3, \mathbf{5}, \mathbf{4}, 6, \ldots)$$

   Such particle systems obey Bose-Einstein statistics and are called **bosons**.

nucleus	I	m_I	
^{1}H	$^{1}/_{2}$	$+^{1}/_{2}, -^{1}/_{2}$	fermion
^{2}H	1	+1, 0, -1	boson
^{3}H	$^{1}/_{2}$	$+^{1}/_{2}, -^{1}/_{2}$	fermion
^{4}He	0	0	boson
^{6}Li	1	+1, 0, -1	boson
^{7}Li	$^{3}/_{2}$	$+^{3}/_{2}, +^{1}/_{2}, -^{1}/_{2}, -^{3}/_{2}$	fermion
^{12}C	0	0	boson
^{13}C	$^{1}/_{2}$	$+^{1}/_{2}, -^{1}/_{2}$	fermion
^{14}N	1	1, 0, -1	boson
^{15}N	$^{1}/_{2}$	$+^{1}/_{2}, -^{1}/_{2}$	fermion
^{16}O	0	0	boson
^{35}Cl	$^{3}/_{2}$	$+^{3}/_{2}, +^{1}/_{2}, -^{1}/_{2}, -^{3}/_{2}$	fermion
^{37}Cl	$^{3}/_{2}$	$+^{3}/_{2}, +^{1}/_{2}, -^{1}/_{2}, -^{3}/_{2}$	fermion
	S	m_S	
electron	½	$+^{1}/_{2}, -^{1}/_{2}$	fermion

It is easy to predict which particles fall into which category. If a particle (or an atomic nucleus) has a spin quantum number which is an **integer**, i.e. has one of the values 0, 1, 2, 3, … it is a **boson**. If it has **half-integral** spin $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, … then it is a **fermion**. The above table is from the NMR course hand-out to which the electron has been added as an honorary member as it has a spin but is not a nucleus.

What happens when identical particles get interchanged?

Of the component wave functions that go to make up the total wave function expressed by eqn. (4), which ones will be affected by the 'switching' of identical particles? The vibrational and electronic functions ψ_{vib} and ψ_{el} are not affected provided these functions describe the ground states in each case[3].

We are left with ψ_{rot} and ψ_{ns} which are the two that will be used to make the total wave function Ψ:

$$\Psi = \psi_{\mathrm{rot}} \times \psi_{\mathrm{ns}} \qquad (5)$$

Spin wave functions

The symmetry behaviour of ψ_{rot} (alias Y_{J,M_J}) for different J has just been dealt with, but what about the nuclear spin function ψ_{ns}? We answer by going straight to a molecular example, H_2. This molecule contains two protons each of which has a spin quantum number $I = ½$. Just as an electron has spin S = ½ and two spin states defined by $m_s = \pm½$, protons have spin states $m_I = \pm½$. Quantum states are characterized by wave functions, and recalling our discussion of the excited singlet and triplet states of the helium atom, we call the two spin state functions α and β just as for electrons. As in the helium problem, the spin function for two particles are written as products of the one-particle functions α and β. Writing $\alpha(1)$ and $\beta(1)$ for the spin wave functions of the proton in hydrogen atom 1 and similarly for the spin functions of proton 2 then the nuclear spin wave functions of the H_2 molecule must be one of the following:

$$\psi_+ = \alpha(1)\alpha(2) \qquad (I = 1 \quad M_I = +1)$$

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[3] Recall that the ground vibrational state $n = 0$ (that accommodates the vast majority of molecules at normal temperatures) is described by a symmetric harmonic oscillator function. You may also remember that the ground state electronic wave function of some molecules considered in our quantum chemical course are totally symmetric, like Ψ_0 in pentalene (A_{1g}) when we were considering allowed transitions between proposed states. Things are not always as simple as the rather cavalier discussion given here pretends, but the reasoning is correct for the ground electronic and vibrational states of most molecules.

$$\psi_+ = \sqrt{\frac{1}{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \qquad (I = 1 \quad M_I = 0)$$

$$\psi_+ = \beta(1)\beta(2) \qquad (I = 1 \quad M_I = -1)$$

$$\psi_- = \sqrt{\frac{1}{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \qquad (I = 0 \quad M_I = 0)$$

These are the possible ψ_{ns} nuclear spin wave functions needed in eqn. (5). The three ψ_+ functions describe a 'proton spin triplet' and ψ_- is a 'proton spin singlet'. Notice that the ψ_+ functions are *symmetric* to interchange of protons 1 and 2 while ψ_- is *antisymmetric* to the interchange. But it is the *total* wave function Ψ that enjoys the property of being invariantly symmetric or antisymmetric, and Ψ is a product of two parts each of which may be *either* symmetric *or* antisymmetric.

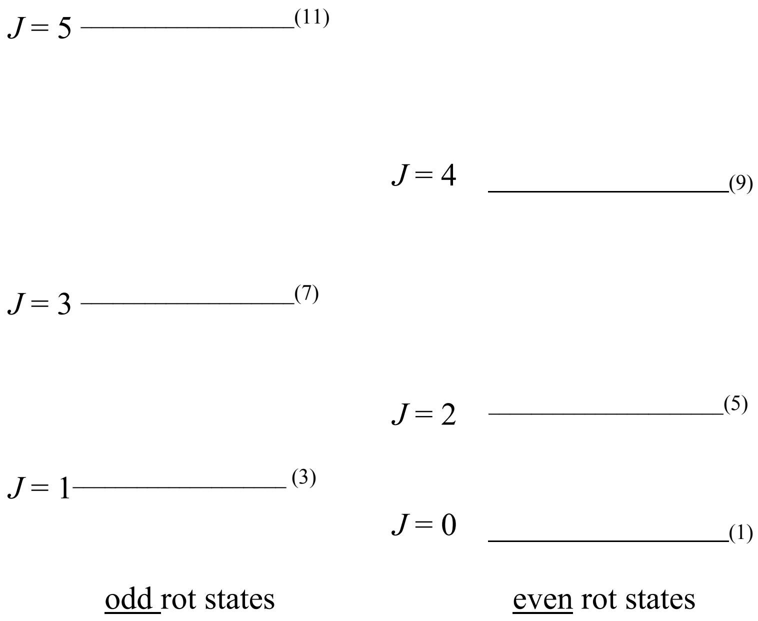
A proton is a fermion, so the total wave function Ψ of the H_2 molecule must be antisymmetric. In order to ensure this the two functions forming the product $\Psi = \psi_{rot} \times \psi_{ns}$ must have different parities – one must be symmetric, the other antisymmetric. If the H_2 molecule is in a rotational state defined by $J = 0, 2, 4, 6, \ldots$ its rotational function is even (symmetric) and so it requires the antisymmetric spin function ψ_-. If it is in a state with $J = 1, 3, 5, \ldots$ then its spin function must be one of the ψ_+ set. An important point is this:

If the spins of the H_2 protons are unpaired, forming a triplet state (ortho hydrogen) then the even-*J* rotational levels do not exist.

If the spins of the H_2 protons are paired, forming a singlet state (para hydrogen) then the odd-*J* rotational levels do not exist.

Thus there are two species of hydrogen molecule, which are called **ortho hydrogen** and **para hydrogen** and they are defined in the two last statements. Their existence is an example of the subject of **spin isomerism**. We now see that the earlier rotational energy diagram which is commonly used to describe the rotation of linear molecules is *wrong* for H_2, and must be replaced by one in which half the rotational levels are missing.

The rotational energy levels in the hydrogen molecule
(Numbers in brackets indicate the degeneracy of the *J* level)



ortho-H_2
(proton spin triplet)

spin functions:
$\alpha(1)\alpha(2)$ $m_I = +1$
$\alpha(1)\beta(2) + \alpha(2)\beta(1)$ $m_I = 0$
$\beta(1)\beta(2)$ $m_I = -1$
$\mathbf{I}_{tot} = 1$

para-H_2
(proton spin singlet)

spin functions:
$\alpha(1)\beta(2) - \alpha(2)\beta(1)$ $m_I = 0$
$\mathbf{I}_{tot} = 0$

Experimental aspects

1. Spectroscopy

With half their rotational levels *missing* compared with ‘normal’ molecules, you might expect to find that molecules with spin isomerism should exhibit anomalies in *some* particular property. (Historically of course it was the anomalies that were first discovered, and theory was then invoked to explain them.)

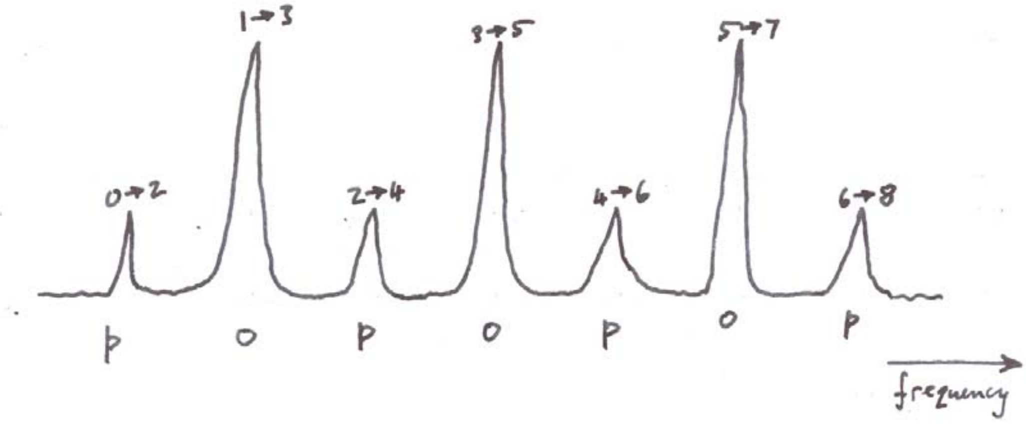
Spectroscopic transitions between rotational levels occur in the microwave region of the spectrum, but such methods cannot be deployed here for the obvious reasons that

(1) in microwave spectroscopy, a molecule giving showing pure rotational transitions **must have a permanent electric dipole moment** which cannot be the case if the molecule has a centre of symmetry, and

(2) sets of levels for which alternate *J*s are missing cannot give rise to the selection rule in microwave spectroscopy, $\boldsymbol{\Delta J = 1}$.

However there are spectroscopsies for which a permanent molecular dipole moment is not required (recall that for an IR vibrational mode to be active it is necessary only that it should have an oscillating dipole moment). *Electronic* transitions don't even need that, and the H_2 molecule does have a UV spectrum.

Electronic energy levels are split by the molecule's vibration, and for a gaseous sample the vibrational levels may be split into rotational levels. The UV spectrum of H_2 does indeed show clear evidence of these missing levels, and can be interpreted as a superposition of molecules for which $J = 0, 2, 4, 6, \ldots$ and for which $J = 1, 3, 5, 7, \ldots$ The H_2 species giving rise to the superposition can be distinguished from their intensities. Except at low temperatures the rotational states would accommodate roughly the same numbers of ortho and para H_2. But when we come to take account of spin it must be considered the components of the spin triplet takes three times as many molecules as the singlet: accordingly at normal temperatures there will be three times as many ortho molecules as para, and the lines originating in ortho-H_2 will show three times the intensity of the para-H_2 lines. As a result the rotational lines will alternate with a 1:3 intensity pattern as shown in the figure[4]:



Raman spectroscopy does not involve electric dipole transitions. Thus no electric dipole moment is required; the principal selection rule here is $\Delta J = 2$, and so Raman spectra also reveal the anomalous rotational energy levels of H_2 and give rise

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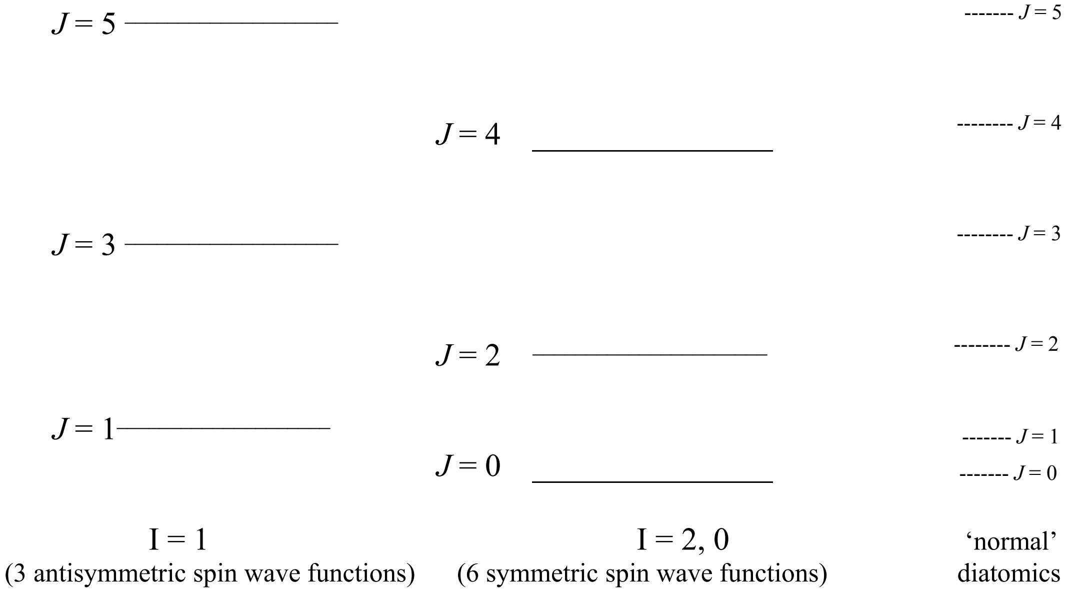
[4] You should remember that even for molecules that don't show spin-rotation effects the rotational lines do not have equal intensities. The amplitudes build up to a maximum and then decrease because of *J*-degeneracy and the Boltzmann effects. In the interests of simplicity this has been neglected here.

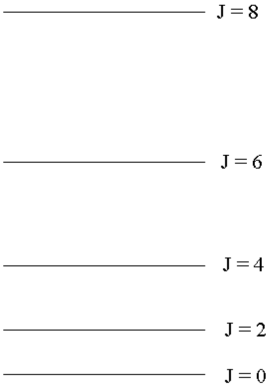
to the 3:1 alternating intensity pattern. It is easy to see that the rotational lines in D_2 and N_2 also have alternating intensities, for which the ratio is 2:1.

The rotational energy levels in a boson molecule (e.g. D_2, $^{14}N_2$ or CO_2)



Abundance ratio at normal temperatures: 1 : 2

In molecules with zero spin, such as $^{16}O_2$ or CO_2 where I = 0 for each ^{16}O , in order for the whole molecular wave function to be symmetric, the rotational functions can only be *even*, and so the energy structure looks like this:



O_2 molecule

(or CO_2)

2. Thermodynamics

Thermodynamic functions such as Heat capacity, Enthalpy, Entropy and Free Energy can be expressed in analytic forms involving *partition functions q*. For example the Helmholtz free energy F of a system of N molecules at a temperature T is given by $F = -NkT[\ln q - \ln N + 1]$. The molecular partition function q depends on the type of motion being considered but if the molecule has a set of quantized energy levels ε_1, ε_2, ε_3, … then it is expressed as $q = e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT} + e^{-\varepsilon_3/kT} + \ldots$ Since q and therefore the system's derived thermodynamic functions depend on the energy levels ε_1, ε_2, ε_3, … the variation of these levels between the spin spin isomers (ortho and para H_2) leads to distinguishable thermodynamic properties.

One of these properties is that concerning phase transition temperatures: the hydrogen molecule is so mobile that the rotational states are said to persist even in the liquid and solid states, and slight differences in the freezing points have been registered for the spin isomers — 13.94 K for ortho and 13.81 K for para.

3. Separation

Since it has just been argued that the ortho and para spin isomers can be distinguished by their thermodynamics, it might be possible to devise a way to separate them using these properties. One obvious way is to use their differing freezing and boiling points. Another is to use their different retention times on alumina; if H_2 gas were passed down an alumina-packed column this gas chromatographic method allows the separation of the ortho and para species.

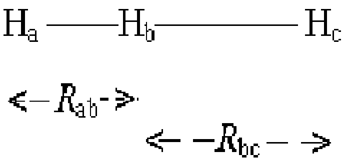
If a sample of hydrogen gas were to be cooled to very low temperatures, nearly all the ortho species would occupy the $J = 1$ level while almost all the para would go into $J = 0$. So ortho-H_2 has zero point energy but not para-H_2, which can have zero rotational energy. At low temperatures, therefore, **para has lower energy than ortho**, and so as an exothermic change a conversion from ortho to para would be energetically favoured. But a mechanism for the conversion would be required. How could a H_2 molecule change from an S=1 proton spin triplet to an S=0 proton singlet?

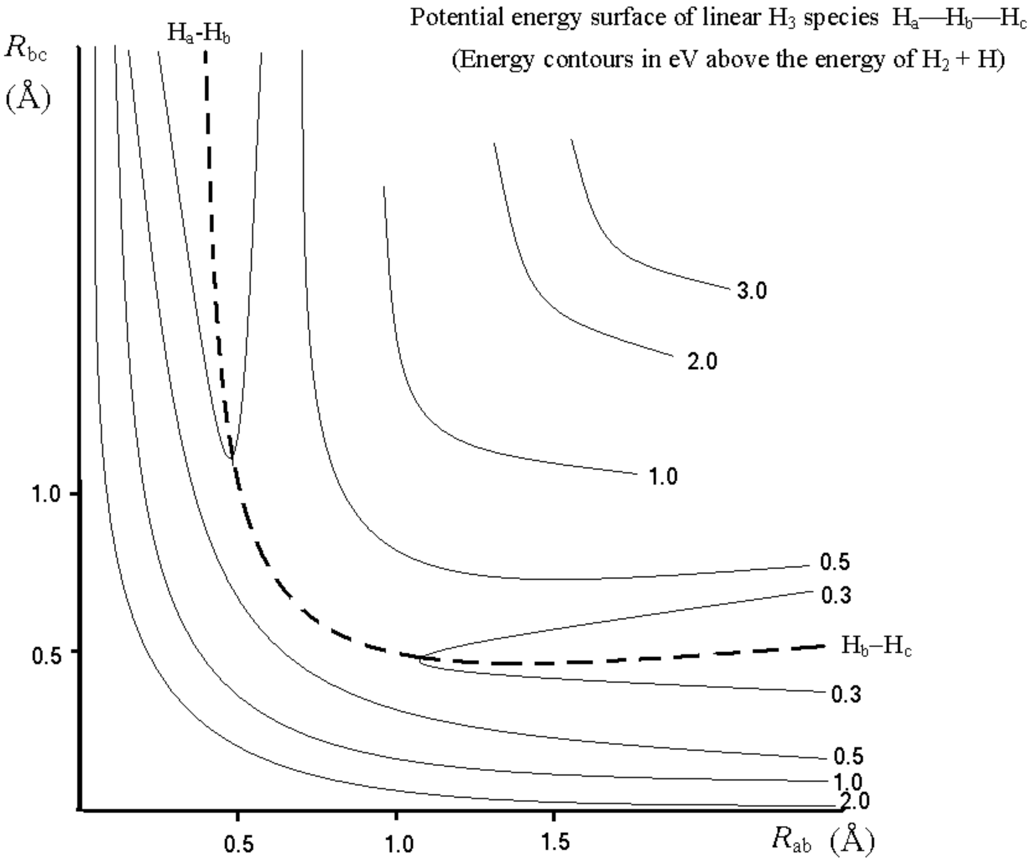
The answer is to use whatever changes particle spin. This is what happens in NMR spectroscopy, which you recall measures the energy absorbed when a proton (or other nucleus) changes its spin from $m_I = +½$ to $m_I = -½$. The transition is induced by supplying radiation at the appropriate frequency (in this case in the radiofrequency range ~10^8 Hz). In proton magnetic resonance this works because **the proton's spin magnetic moment couples with the radiation's oscillating magnetic field**. The oscillating field induces transitions between the $m_I = \pm½$ states in either direction.

If an oscillating magnetic field at the appropriate frequency were applied to a H_2 spin isomer it could be converted into the other isomer. But it is not necessary to do this. Spin-flip transitions may occur independently of applied radiation due mainly to background magnetic fields arising from proton spin dipoles in other H_2 molecules. These fields fluctuate as a result of H_2 molecular collisions. As random processes the frequencies of the fluctuations will be very wide, but will probably contain a component at the 'resonance' value, and will therefore be instrumental in inducing the $m_I = \pm½$ state transitions. Again, the transitions may go in either direction, but as a transition from a higher to a lower energy state is more probable than the other way round, H_2(ortho) → H_2(para) is favoured over the reverse reaction, and eventually (months) our low-temperature H_2 sample would end up pure para.

But there are speedier methods. One is to use a catalyst for the dissociation of H_2 into H atoms and reassembly to H_2. At very low temperatures thermodynamics favours the $H + H \rightarrow H_2$(para) over $H + H \rightarrow H_2$(ortho) as it is more exothermic. Another way is to add a small paramagnetic gaseous impurity to the H_2 sample. As the paramagnetic molecule collides with H_2 molecules, and if the frequency spread of the fluctuating magnetic fields thereby generated contain a component at the right frequency, spins would be flipped and the sample would go over into para hydrogen. Then again, rather than add a gaseous impurity, if the vessel containing the hydrogen sample were glass containing (as glass often does) paramagnetic ions like Fe^{3+}, the required spin flips would still occur — this time because of the fluctuating magnetic fields experienced by the H_2 molecules as they collide with a range of speeds and directions with the walls of the container.

One purpose in being able to prepare pure spin rotamers is to provide an experimental means to study the kinetics of the reaction $H_2 + H \; = \; H + H_2$ which has been the subject of many theoretical investigations. Its progress will be a line on the potential energy surface of H_a—H_b—H_c shown below where it is assumed that the H_3 reaction intermediate is linear. The reaction will follow some pathway from the (H_a–H_b + H_c) valley, over the saddle-point energy barrier to the symmetrically equivalent (H_a + H_b–H_c) valley. A gaseous system of pure para H_2 and atomic hydrogen will undergo a scission of H–H bonds of the para H_2 reactant molecules to form H_2 product molecules which, when equilibrium is reached, will be in the ratio of ortho : para = 3 : 1. Measuring the proportion of ortho and para molecules in the system allows the progress of the reaction to be monitored, and a measurement of the rate constant *k*. Measuring *k* as a function of temperature and using the Arrhenius equation $k = Ae^{-E^*/kT}$ enables the activation energy E^* to be calculated from the plot of ln *k* *vs* 1/*T*.





The broken line is the lowest-energy trajectory (reaction coordinate) in between (H_a–H_b + H_c) and (H_a + H_b–H_c) in which the H atom approaches 'in line' with the molecule.