

Wavefunction symmetry – homonuclear diatomic molecules

Total wavefunction of the molecule must fulfill requirements on the symmetry of the nuclear interchange.

- nuclei with half-spin must change the sign

Nuclei interchange ~ (1) inversion of all particles (el. + nuc.)
 (2) inversion of electrons back

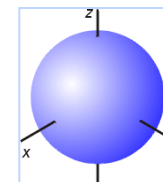
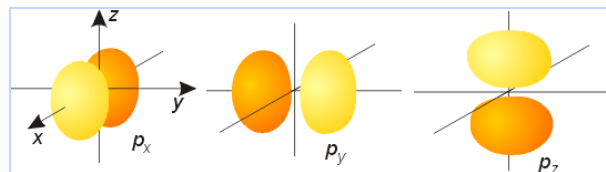
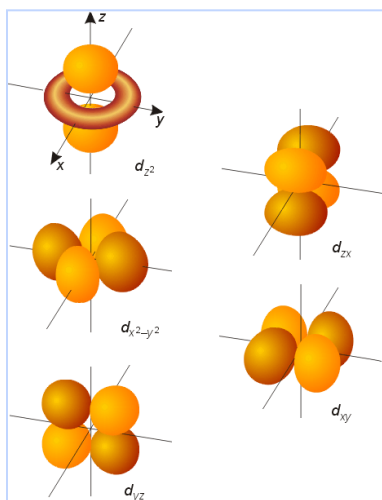
$$\psi'_{total} = \psi_{trans} \psi_{vib} \psi_{rot} \psi_{elec}$$

Symmetric

Change the sign for „ungerade“ wf
 Closed-shell molecules – “gerade” – no change

Determines the overall symmetrical properties

Eigenfunctions of rigid rotor = angular fce of H atom
 ψ_{rot} – changes the sign for odd J



H₂ molecule in the electronic ground state – nuclei spin of $I = \frac{1}{2}$

Just like for the wavefunction of singlet and triplet:

Symmetric wavefunctions

$$\alpha\alpha, \beta\beta, \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha)$$

Statistical weight 3

Antisymmetric wavefunction

$$\frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

Statistical weight 1

Overall wavefunction must be antisymmetric:

⇒ Rotational states with even J – couples with the antisymmetric spin (nuclei) function

⇒ Rotational states with odd J – couples with symmetric spin function

Ortho-hydrogen (parallel nuclei spin) vs. Para-hydrogen (opposite spin on nuclei)

Diatomics – in general

Nucleus with the spin I - $2I + 1$ spin states

Homonuclear diatomics: $(2I+1)^2$ nuclear wavefunctions
 $(2I+1)(2I)/2$ - antisymmetric nuclear spin functions
 $(2I+1)(I+1)$ - symmetric ...

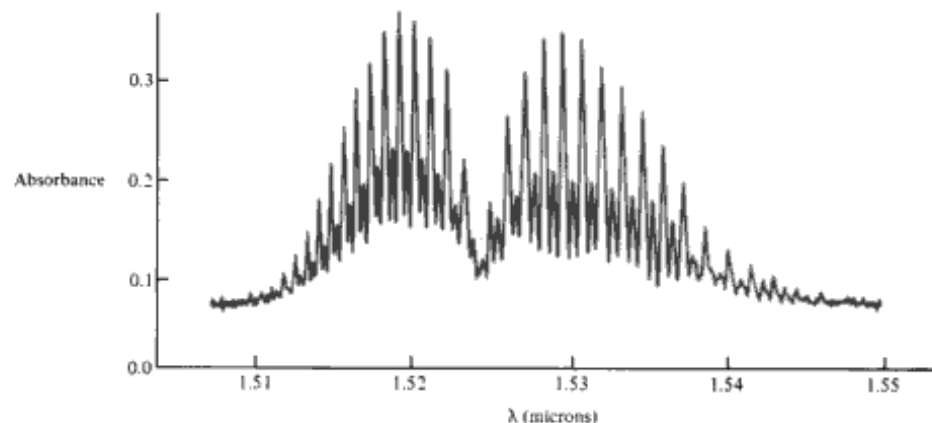


Figure 6-7. The vibration-rotation spectrum of acetylene. This represents one vibrational line. The alternation in the intensity of the lines is due to the statistical weights of the rotational levels. (From L. W. Richards, *J. Chem. Ed.*, 43, p. 645, 1966.)

Summary for electronic ground state with symmetrical inversion

Half-integer spin

$I(2I+1)$ antisymmetric nuclear spin functions couple with even J

$(I+1)(2I+1)$ symmetric nuclear spin functions couple with odd J

Integer spin

$I(2I+1)$ antisymmetric nuclear spin functions couple with odd J

$(I+1)(2I+1)$ symmetric nuclear spin functions couple with even J

Platí i pro ostatní lineární molekuly se středem inverze

Summary for electronic ground state with symmetrical inversion

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Rotational and nuclear partition functions are coupled ! (cannot be separated)

Molecules with integral spin

$$q_{rot,nucl}(T) = \frac{I+1}{2I+1} \sum_{J_{even}} 2J+1 e^{-\Theta_r J(J+1)/T} + \frac{I}{2I+1} \sum_{J_{odd}} 2J+1 e^{-\Theta_r J(J+1)/T}$$

Molecules with half-integral spin

$$q_{rot,nucl}(T) = \frac{I}{2I+1} \sum_{J_{even}} 2J+1 e^{-\Theta_r J(J+1)/T} + \frac{I+1}{2I+1} \sum_{J_{odd}} 2J+1 e^{-\Theta_r J(J+1)/T}$$

$$\Theta_r \ll T$$

Simplification

$$\sum_{J_{\text{even}}} \approx \sum_{J_{\text{odd}}} \approx \frac{1}{2} \sum_J \approx \frac{1}{2} \int_0^{\infty} 2J+1 e^{-\Theta_r J(J+1)/T} dJ = \frac{T}{2\Theta_r}$$

$$q_{\text{rot,nucl}}(T) = \frac{(2I+1)^2 T}{2\Theta_r}$$

$$q_{\text{nucl}}(T) = (2I+1)^2$$

$$q_{\text{rot}}(T) = \frac{T}{2\Theta_r}$$

„Symmetry number“ - 1 for heteronuclear molecules
2 for homonuclear

~~$$\Theta_r \ll T$$~~

H_2 $I = 1/2$, Σ_g^+

$$q_{\text{rot,nucl}}(T) = I(2I+1) \sum_{J_{\text{even}}} 2J+1 e^{-\Theta_r J(J+1)/T} + (I+1)(2I+1) \sum_{J_{\text{odd}}} 2J+1 e^{-\Theta_r J(J+1)/T}$$

$$q_{\text{rot,nucl}}(T) = \sum_{J_{\text{even}}} 2J+1 e^{-\Theta_r J(J+1)/T} + 3 \sum_{J_{\text{odd}}} 2J+1 e^{-\Theta_r J(J+1)/T}$$

para

ortho

| Molekula | El. stav | B cm^{-1} | Θ_r (K) |
|--------------|---------------|--------------------|----------------|
| H_2 | $1\Sigma_g^+$ | 59.3 | 85.3 |

Higher than boiling temperature
Numerical solution - MATLAB

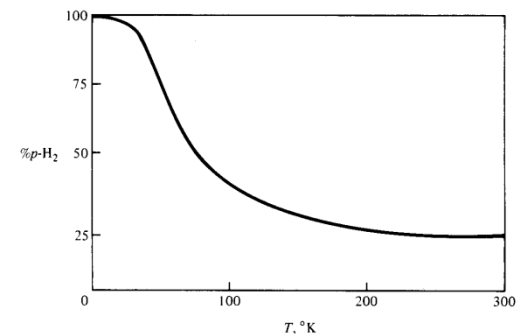


Figure 6-8. The percentage of para-hydrogen in an equilibrium mixture as a function of temperature.

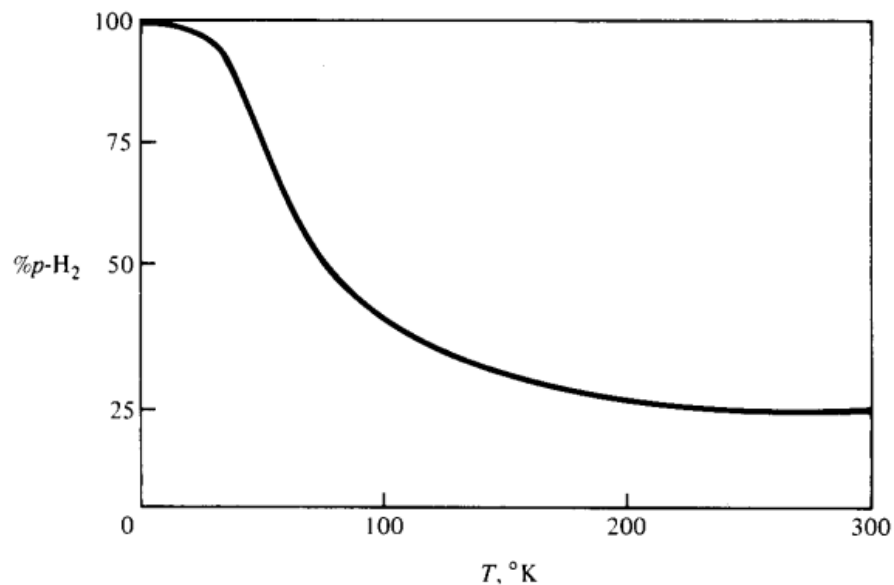
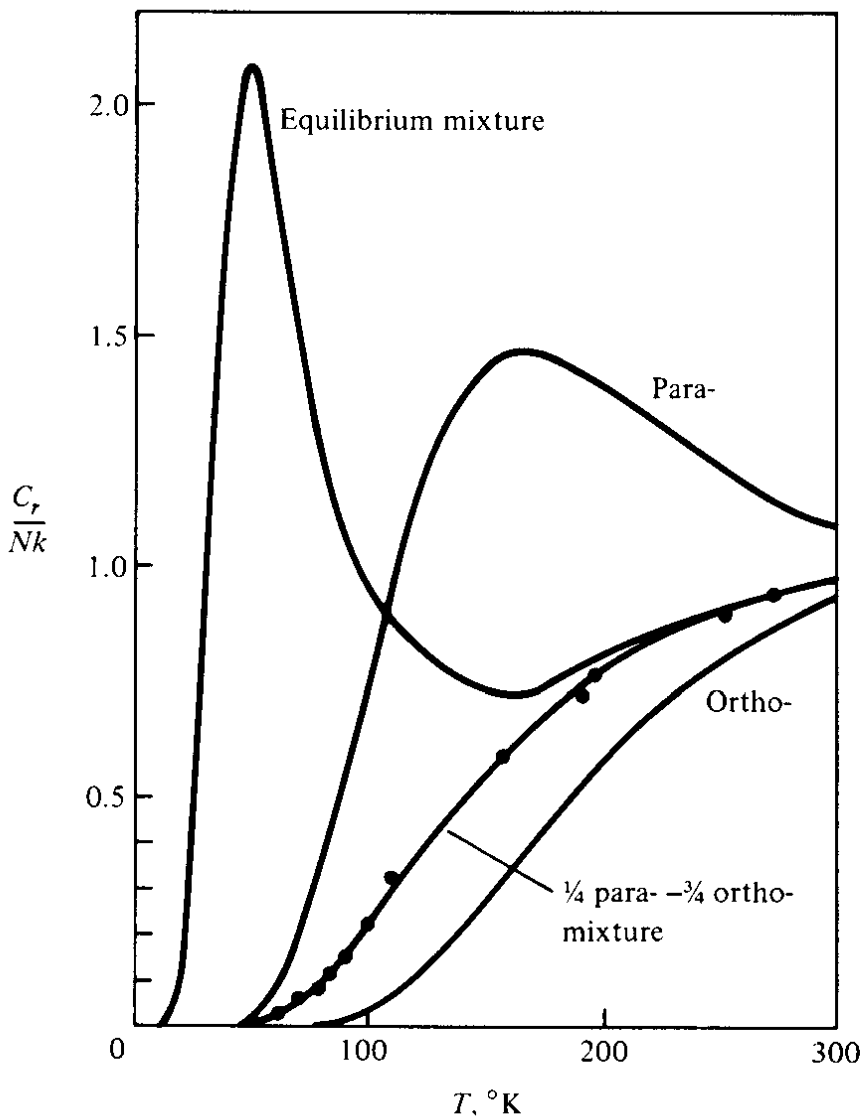


Figure 6-8. The percentage of para-hydrogen in an equilibrium mixture as a function

From McQuarrie

Figure 6-9. The rotational and nuclear contribution to the molar heat capacity for ortho-hydrogen, para-hydrogen, an equilibrium mixture of ortho- and para-hydrogen, a metastable 75 percent ortho- and 25 percent para- mixture, and the experimental data. (From K. F. Bonhoeffer and P. Harteck, *Z. Physikal. Chem.*, **4B**, p. 113, 1929.)

Total partition function for diatomics:

$$q(V, T) = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \omega_e e^{D_e/kT}$$

$$\Theta_r \ll T$$

Simple models

$$\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \frac{D_e}{kT}$$

Possible improvements:

Anharmonic treatment of vibrational motion

Centrifugal distortion

Rotational-vibrational “bond” - coupling

$$\varepsilon_{vr} = (n + \frac{1}{2})h\nu + \bar{B}J(J+1) - x_e(n + \frac{1}{2})^2 h\nu - \bar{D}J^2(J+1)^2 - \alpha(n + \frac{1}{2})J(J+1)$$

$$q(V, T) = q_{rr} q_{ho} q_{corr}$$

$$q_{corr} = 1 + \frac{2kT}{\bar{B}} \left(\frac{\bar{D}}{\bar{B}} \right) + \frac{1}{e^{\beta h\nu} - 1} \left(\frac{\alpha}{\bar{B}} \right) + \frac{2\beta h\nu}{e^{\beta h\nu} - 1} x_e$$

And higher order corrections

Molecules with low-lying electronic states (radicals)

Several electronic states should be included in the partition functions

Molecules with other than Σ electronic ground state

Electronic and rotational angular momenta are coupled

$q_{el,r}$