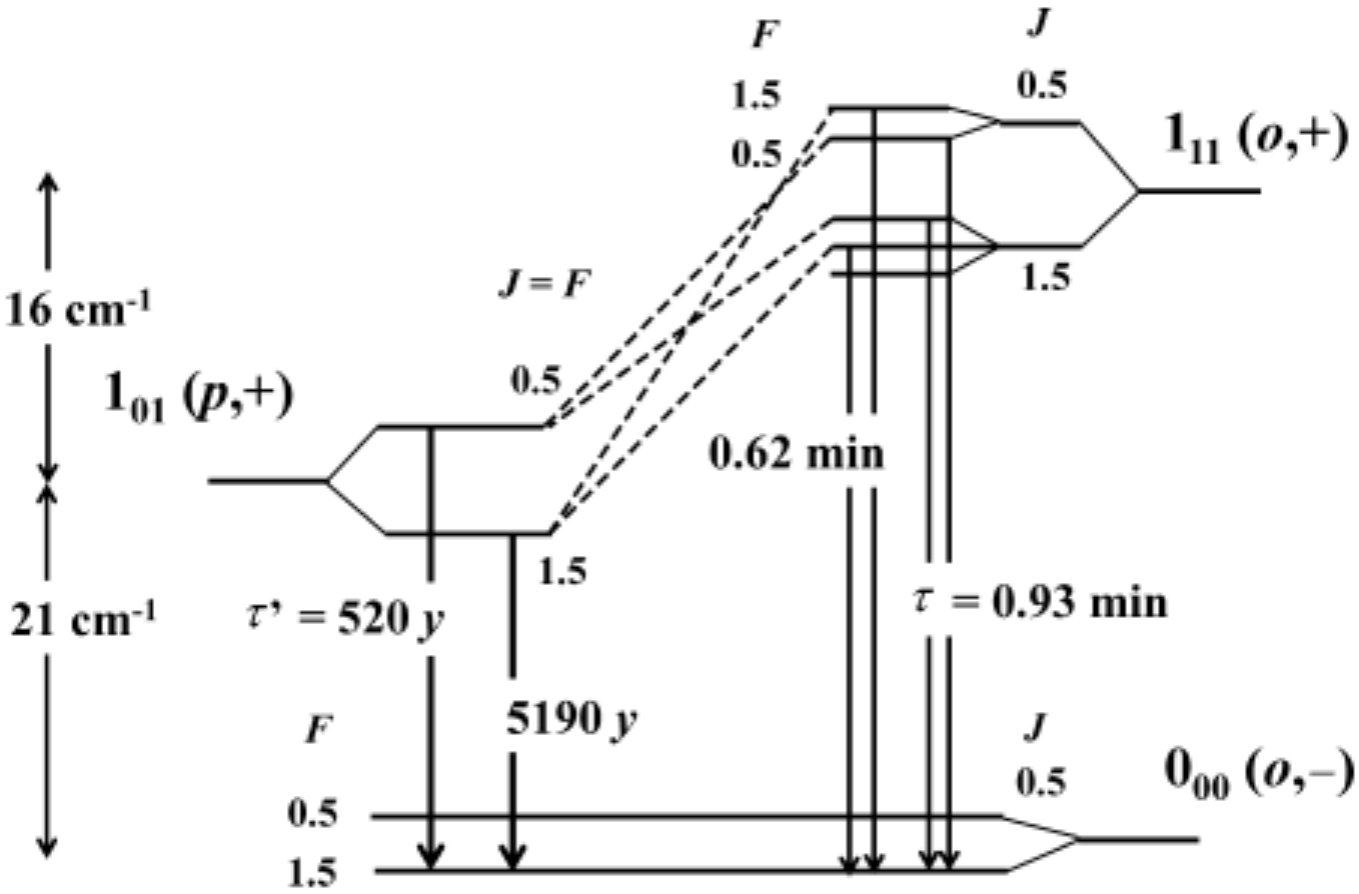
(3) Conservation and variation of spin isomers by collision and radiation

September 27, Tuesday 10:30 -



Ortho/Para He

H_2

Tomonaga

H_2O, H_2CO
NH_3, CH_3OH,
CH_4, C_2H_4

H_3^+

Handbook

1895 Runge and Paschen. Spectra of He and "parhelium". [ApJ, 3, 4 (1896)].
1912 Eucken. Anomalous specific heat for H_2 (Sitzber. Preuss. Akad. Wiss. 41).
1922 Gerlach and Stern. Experimental proof of space quantization (ZPhy 9, 349).
1922 A. Fowler. Use of ortho-helium and parhelium as recommendation by Bohr.
1924 Pauli. Introduction of nuclear spin for hyperfine structure (NW 12, 742).
Mecke. Discovery of intensity alternation in N_2^+ spectrum (ZPhy 28, 261).
1925 Pauli. *ad hoc* exclusion principle (ZPhy 31, 765).
Uhlenbeck and Goudsmit. Introduction of electron spin (NW 13, 953).
1926 Heisenberg (ZPhy 38, 41). Dirac (Proc. R. Soc. A112, 661). Deeper formulation of Pauli's Exclusion Principle. Heisenberg explains ortho and para helium.
1927 Heisenberg. Ortho-H_2 (J odd) and para-H_2 (J even) (ZPhy 41, 239).
Hori. Observation of 3:1 intensity alterations in H_2 spectrum (ZPhy 44, 834).
Dennison. Stable o-, p-H_2 to explain the specific heat (Proc. R. Soc. A115, 483).
1929 Bonhoeffer and Harteck. Preparation of pure para-H_2 (ZPhy Chem. B4, 113).
1933 Wigner. Theory for the stability of ortho and para H_2 (ZPC B23, 28)
Mecke. Observation of intensity alternation in H_2O (ZPhy 81, 313).
1940 Pauli. Theoretical proof of Pauli's exclusion principle (PhRv 58, 716).
1964 Raich and Good. Ortho→para H_2 spontaneous emission $J = 1 \rightarrow 0$. (ApJ 1389, 1004).
1967 Curl et al. Theory for spin conversion in polyatomic molecules (JChPh 46, 3220).
1968 Oka. Experimental proof for stability of o- and p-NH_3 (JChPh 49, 3135).
1970 Ozier et al. Observation of o-p transition of CH_4 in magnetic field (PhRvL 24, 642).
1973 Dalgarno et al. Ortho-para conversion of H_2 by reaction with H^+ (ApL 14, 77).
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2013 Tanaka et al. Ortho-para H_2O^+ spontaneous emission (JPCA 117, 9584).
2014 Takagi et al. High spin conversion rate in CH_3OH (private communication).

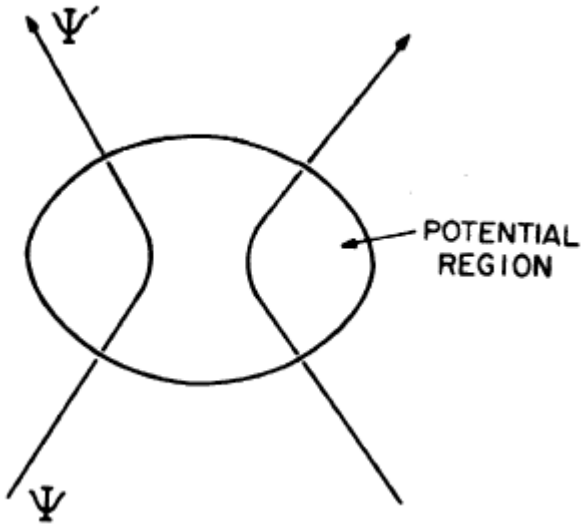
Nuclear spin

Electron spin

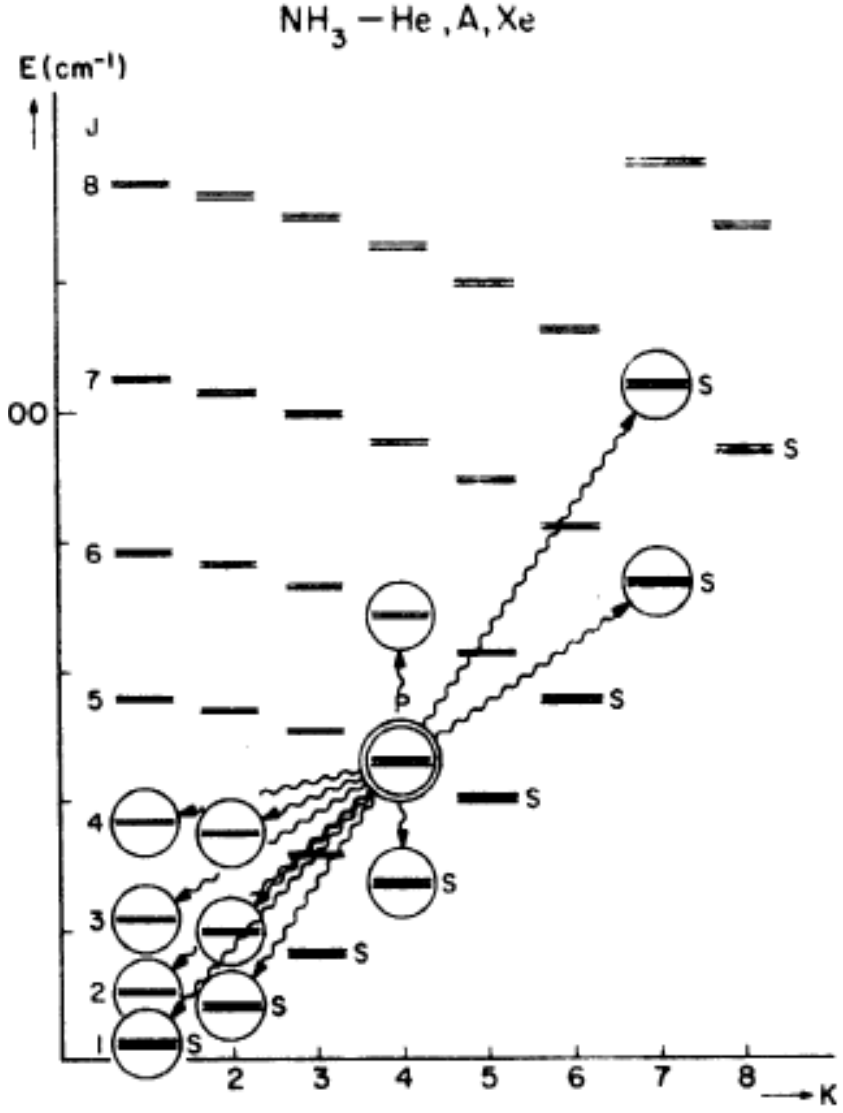
Conservation of ortho- and para-NH_3

$$\left[D_{1/2}\right]^3 = D_{3/2} \oplus 2D_{1/2}$$

ortho $K = 3n$ para $3n \pm 1$



$$\Delta k = 3n$$



Nuclear Spin State Equilibration through Nonmagnetic Collisions

R. F. Curl, Jr., Jerome V. V. Kasper,† and Kenneth S. Pitzer

$$H = H_{\text{rot}} + T_{ab}\left[(I_{1a} - I_{2a})J_b + (I_{1b} - I_{2b})J_a\right]$$

H_2O H_2CO

$$\langle J'K'_-K'_+I'FM_F \mid H \mid J_{K_-K_+}IFM_F\rangle = (-1)^{J+J'+K'_-+I'+F}\{15[J(J+1)(2J'+1)]\}^{1/2}(2J+1)$$
$$\times \begin{Bmatrix} F & I' & J' \\ 1 & J & I \end{Bmatrix} \times \begin{Bmatrix} J' & J & 2 \\ 1 & 1 & J \end{Bmatrix} \times \begin{pmatrix} J' & 2 & J \\ -K'_- & 1 & K_- \end{pmatrix} \times T_{ab},$$

'67 Curl et al. Theory for spin conversion in polyatomic molecules (JChPh 46, 3220).
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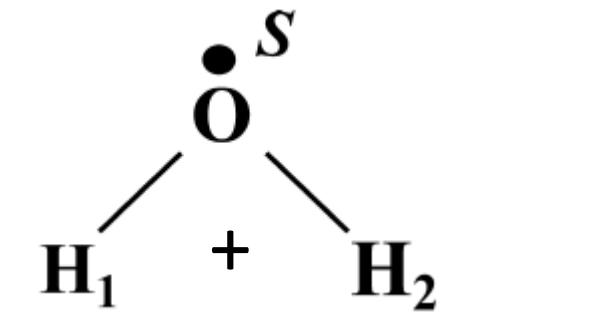
'14 Takagi et al. High spin conversion rate in CH_3OH (private communication).

Ortho–Para Mixing Hyperfine Interaction in the H_2O^+ Ion and Nuclear Spin Equilibration

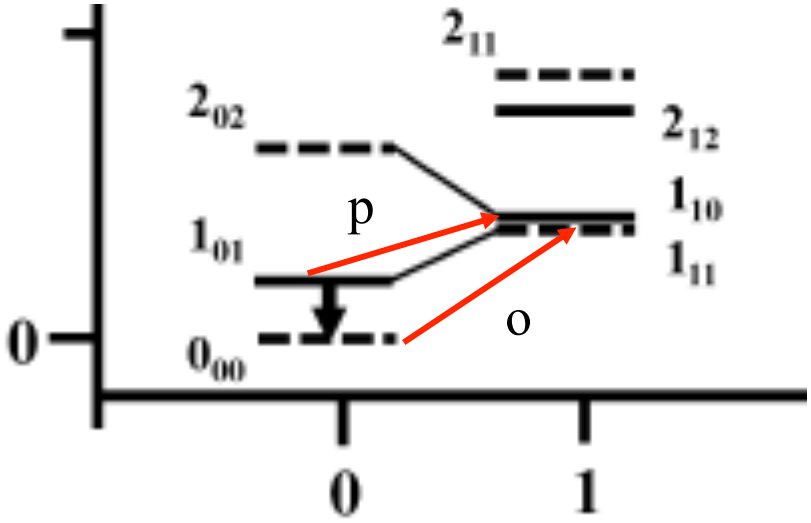
Keiichi Tanaka,*[,†,‡] Kensuke Harada,[‡] and Takeshi Oka[§]

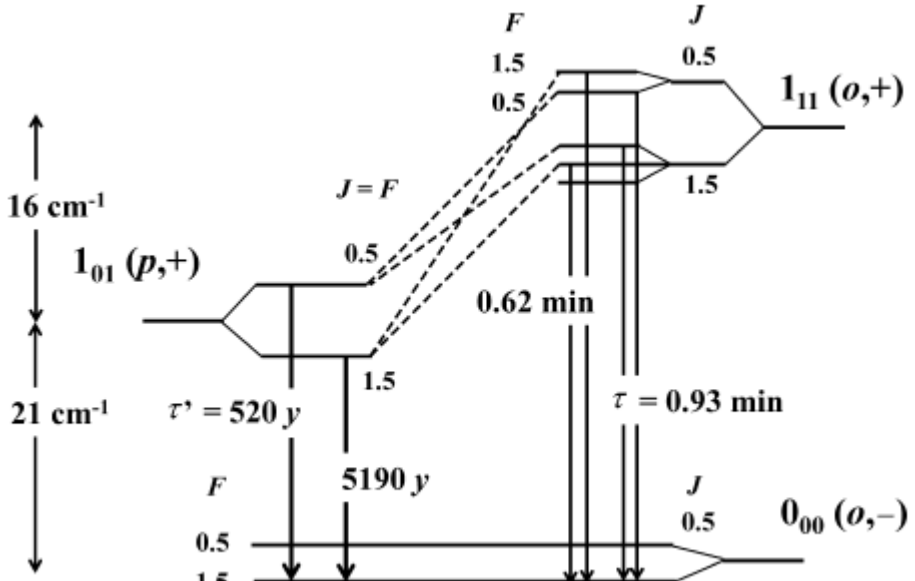
J. Phys. Chem. 117, 9584 (2013)



$$H_1 = T_{ab}S_a(I_{1b} - I_{2b}) + T_{ba}S_b(I_{1a} - I_{2a})$$

$$\begin{aligned}\langle N', K_a', S, J', I', F, M_F|H_1|N, K_a, S, J, I, F, M_F\rangle \\ = -(-1)^{I'+F+J}(30S(S+1)(2S+1)(2N+1) \\ \times (2N'+1)(2J+1)(2J'+1))^{1/2} \\ \times \langle I'||\Delta I^{(1)}||I\rangle \begin{Bmatrix} J' & I' & F \\ I & J & 1 \end{Bmatrix} \begin{Bmatrix} N' & S & J' \\ N & S & J \\ 2 & 1 & 1 \end{Bmatrix} \\ \times \sum_{p=\pm 1} (-1)^{N'-K_a'} \begin{pmatrix} N' & 2 & N \\ -K_a' & p & K_a \end{pmatrix} T_p^{(2)}\end{aligned}$$

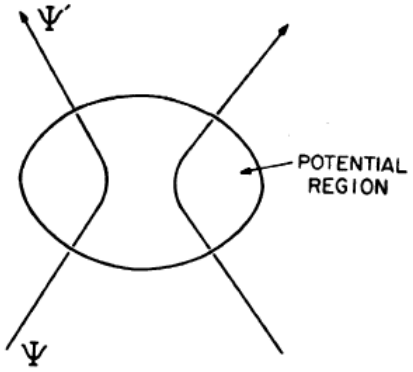


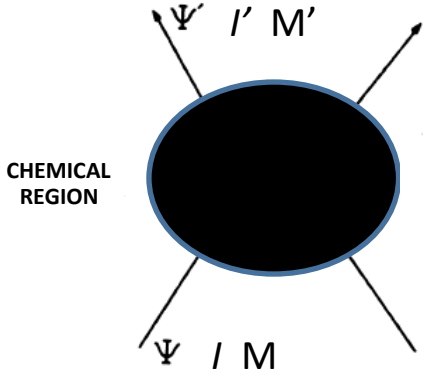


Schilke, P.; Comito, C.; Müller, H. S. P.; Bergin, E. A.; Herbst, E.; Lis, D. C.; Neufeld, D. A.; Phillips, T. G.; Bell, T. A.; Blake, G. A.; et al. Herschel Observations of Ortho- and Para-Oxidaniumyl (H_2O^+) in Spiral Arm Clouds Toward Sagittarius B2(M). *Astron. Astrophys.* **2010**, *521*, L11.

Chemical collisions

Physical collision





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Ortho–Para Transitions in H_2 and the Fractionation of HD

A. DALGARNO, J. H. BLACK, and J. C. WEISHEIT *Harvard College Observatory and Smithsonian Astrophysical Observatory, Cambridge, Massachusetts 02138, USA*

$$\mathrm{H} + \mathrm{o\text{-}H_2} \rightleftarrows \mathrm{H} + \mathrm{p\text{-}H_2}$$

$$\mathrm{o\text{-}H_2} + g \rightleftarrows \mathrm{p\text{-}H_2} + g,$$

$$\mathrm{H^+} + \mathrm{o\text{-}H_2} \rightleftarrows \mathrm{H^+} + \mathrm{p\text{-}H_2}$$

Ammonia formation and the ortho-to-para ratio of H_2 in dark clouds

J. Le Bourlot

DAMAp, Observatoire de Paris/Meudon, Place Jules Janssen, F-92195 Meudon Principal Cedex, France

$$\mathrm{H^+} + \mathrm{H_2}(J=0) \rightarrow \mathrm{H^+} + \mathrm{H_2}(J=1) - 170\ \mathrm{K}$$

$$\mathrm{H_3^+} + \mathrm{H_2}(J=0) \rightarrow \mathrm{H_3^+} + \mathrm{H_2}(J=1) - 170\ \mathrm{K}.$$

Quack, M. (1977) Detailed symmetry selection rules for reactive collisions. *Molecular Physics*, **34**, 477–504.

Observation of Ortho-Para H_3^+ Selection Rules in Plasma Chemistry

Dairene Uy,* Michel Cordonnier,† and Takeshi Oka

$$H_3^+ + \tilde{H}_2 \longrightarrow H_2 + \tilde{H}_2H^+,$$

$$H_3^+ + \tilde{H}_2 \longrightarrow \tilde{H}H_2^+ + H\tilde{H}$$

Nuclear spin selection rules in chemical reactions by angular momentum algebra

Takeshi Oka*

$$\mathscr{D}_{I_1} \otimes \mathscr{D}_{I_2} = \mathscr{D}_{I_1+I_2} \oplus \mathscr{D}_{I_1+I_2-1} \oplus \cdots \oplus \mathscr{D}_{|I_1-I_2|}$$

Frobenius reciprocity