Development of the Physics of Spin Isomers and its Application to Astrochemistry:

(1) The story of spin and spin isomers
(2) Orders of magnitude and symmetry, the two pillars of spectroscopy
(3) Conservation and variation of spin isomers by collision and radiation

Takeshi Oka

Department of Astronomy and Astrophysics and Department of Chemistry
The Enrico Fermi Institute, the University of Chicago

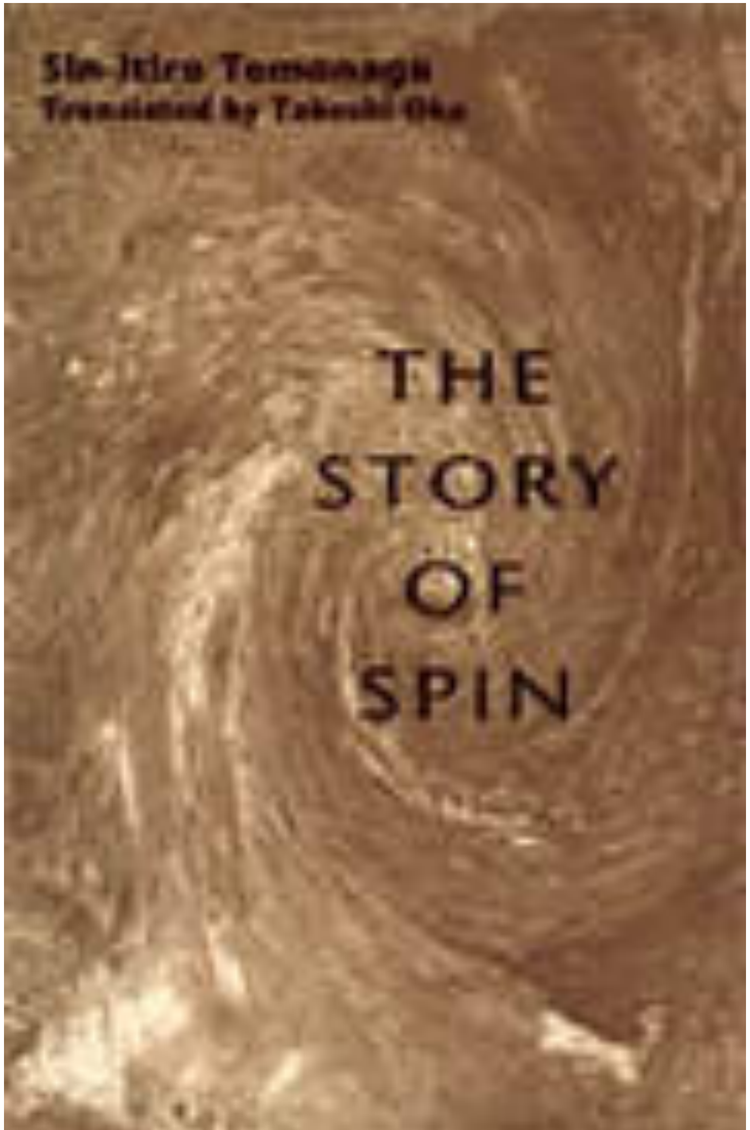
★ S. Tomonaga, *The Story of Spin*, University of Chicago Press (1997)

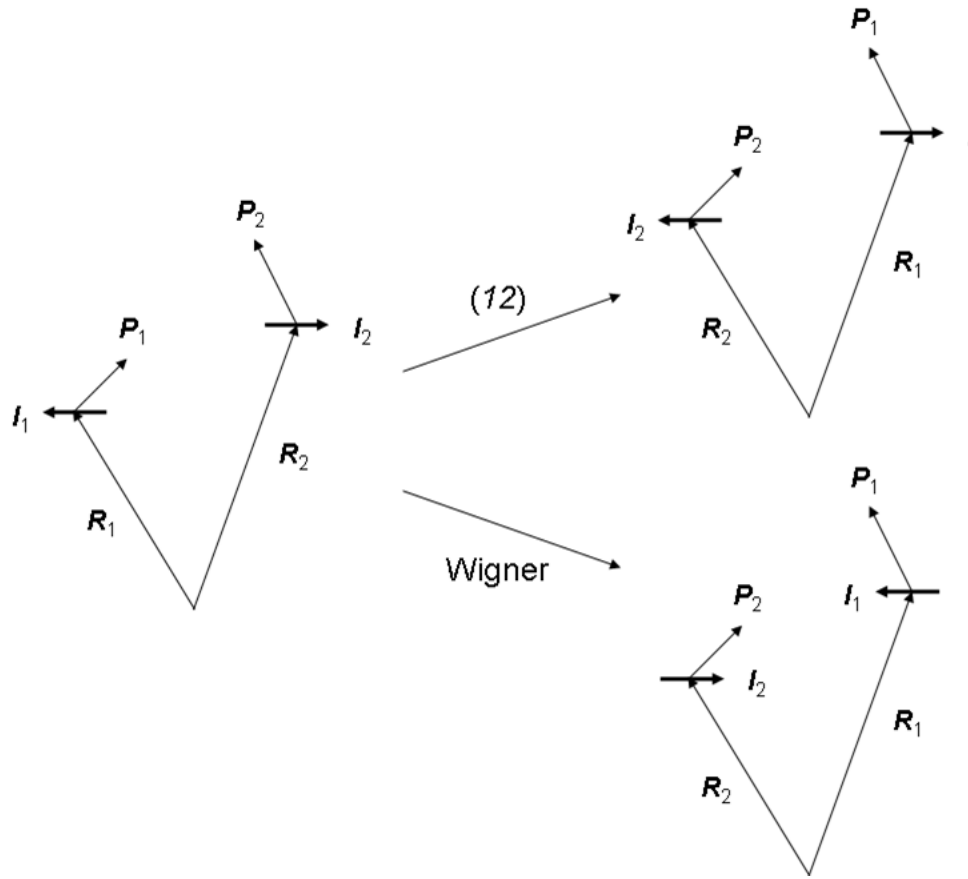
★ T. Oka, *Orders of Magnitude and Symmetry in Molecular Spectroscopy* in Handbook of High Resolution Spectroscopy, Vol. I, John Wiley & Sons (2011)

Zentrum für astrochemische Studien, Max-Planck-Institut für extraterrestrische Physik,
Garching, Germany, September 23 - 27, 2016

(1) The Story of Spin and Spin Isomers

September 23, Friday 10:30 -





The Story of Spin

Sin-itiro (Sin'ichirō) Tomonaga 1906 – 1979
Founder of quantum electrodynamics together with
Julian Schwinger, Richard Feynman Physics Nobel 1965
Freeman Dyson

Ortho/Para He

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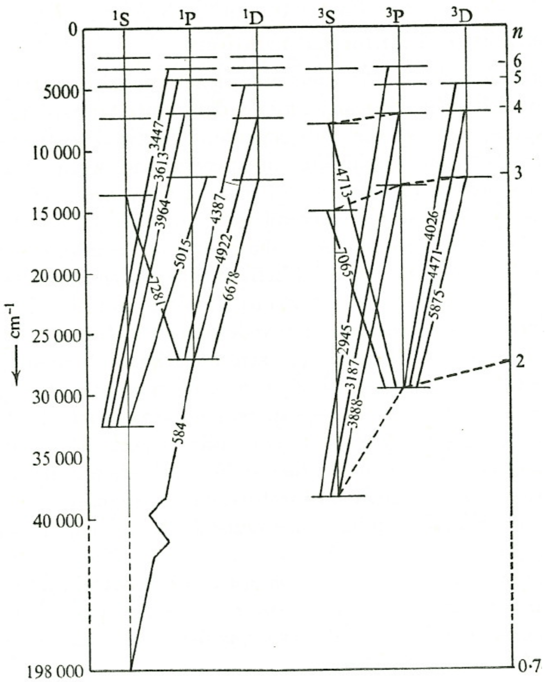
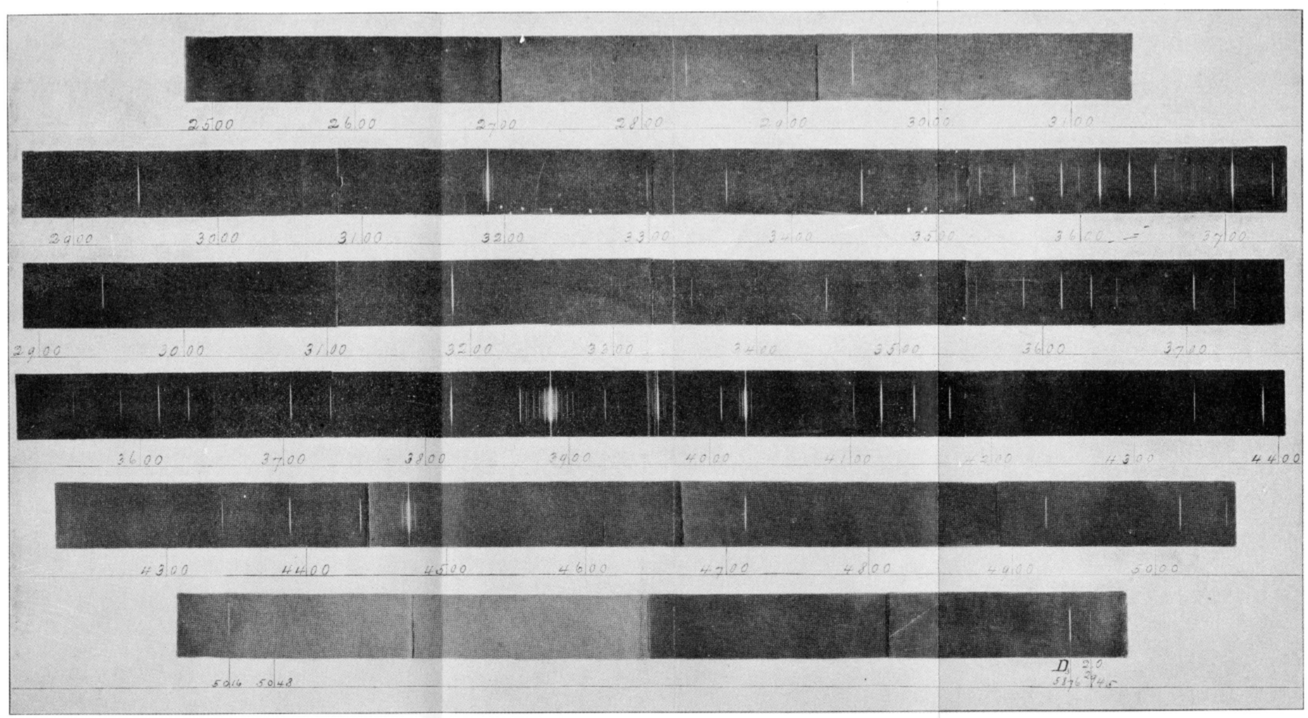
Helium and parhelium

ON THE SPECTRUM OF CLÈVEITE GAS.[1]

By C. RUNGE AND F. PASCHEN. ApJ 3, 4 (1886)



$$\frac{1}{\lambda} = A + \frac{B}{n^2} + \frac{C}{n^3}$$



PHOTOGRAPH OF THE SPECTRUM OF CLÈVEITE GAS TAKEN IN THE FIRST ORDER OF A LARGE ROWLAND CONCAVE GRATING.

There are some impurities visible, principally hydrogen and traces of the cyanogen band 3883 and of nitrogen bands. The strong lines are accompanied by "ghosts" on either side. Two photographs are given of the region from λ2900 to λ3700.

the name *Helium* should be given only to the second element, the spectrum of which includes D_3. The first element Professor Stoney has proposed to call *Parhelium*.[2] In all the spectra of

Pauli's Exclusion Principle

W. Pauli Z. Physik 31, 765 (1925) "We cannot give a more precise reason"

W. Heisenberg Z. Physik 38, 411 39, 499 (1926) 41, 239 (1927)
P. A M. Dirac Proc. Roy. Soc. A112, 661 (1926)

$$(1,2)\Psi(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{I}_1; \boldsymbol{r}_2, \boldsymbol{p}_2, \boldsymbol{I}_2) = \Psi(\boldsymbol{r}_2, \boldsymbol{p}_2, \boldsymbol{I}_2; \boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{I}_1) = -\,\Psi(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{I}_1; \boldsymbol{r}_2, \boldsymbol{p}_2, \boldsymbol{I}_2) \quad \text{for fermion}$$
$$= +\,\Psi(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{I}_1; \boldsymbol{r}_2, \boldsymbol{p}_2, \boldsymbol{I}_2) \quad \text{for bosons}$$

Self-effacing Dirac

Heisenberg's equation of motion (1925)
Pauli's exclusion principle (1926)
Einstein's coefficient (1927)
Fermi's golden rule (1927)

W. Pauli, Phys. Rev. 58, 716 (1940)

The most subtle and ingenious design of nature

Why is it that particles with half-integral spin are Fermi particles whose amplitudes add with the minus sign, whereas particles with integral spin are Bose particles whose amplitudes add with the positive sign? We apologize for the fact that we cannot give you an elementary explanation. An explanation has been worked out by Pauli from complicated arguments of quantum field theory and relativity. He has shown that the two must necessarily go together, but we have not been able to find a way of reproducing his arguments on an elementary level. It appears to be one of the few places in physics where there is a rule which can be stated very simply, but for which no one has found a simple and easy explanation. The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved. For the moment, you will just have to take it as one of the rules of the world.

The Feynman Lectures on Physics Vol. 3, p 4-3

S. Tomonaga, *The Story of Spin*, University of Chicago Press (1997)

I. Duck & E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*
World Scientific, Singapore (1997)

The all mighty formula

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

Landau Lifshitz, Vol. 3 "Quantum Mechanics: non-relativistic Theory"
Pergamon, 1977 § 106

$$\left[D_{1/2}\right]^2 = D_1 \oplus D_0$$

The principle of superposition of states

The Nobel Prize in Physics 1932
Werner Karl Heisenberg

"for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"

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Stability of ortho and para H_2; Wigner's near symmetry

Über die paramagnetische Umwandlung von Para-Orthowasserstoff. III.

Von

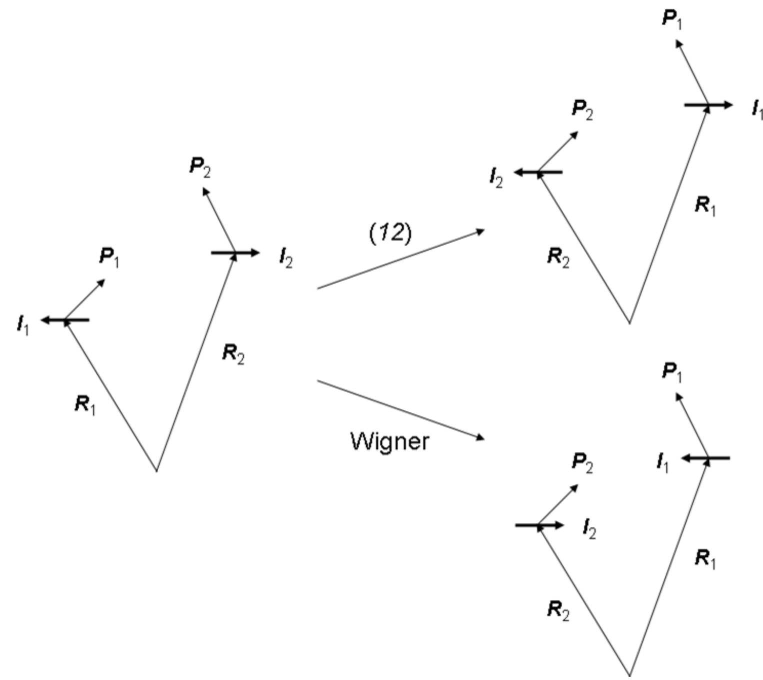
E. Wigner.

(Aus dem Kaiser Wilhelm-Institut für physikalische Chemie und Elektrochemie, Berlin-Dahlem.)

Z. Physik. Chem. B23, 28 (1933)

Die besondere Stabilität des Parawasserstoffes beruht auf einer Symmetrieeigenschaft des quantenmechanischen Energieoperators für das Wasserstoffmolekül: Er bleibt nicht nur dann ungeändert, wenn man sämtliche Koordinaten der beiden Protonen vertauscht, sondern näherungsweise auch schon dann, wenn man ihre Cartesischen Koordinaten allein vertauscht, während die Spinkoordinaten ungeändert bleiben können.

"the special stability of para-H_2 is based on a symmetry property of the quantum mechanical energy operator of the hydrogen molecule; it is not only invariant when the entire set of coordinates of both protons are exchanged but also *nearly invariant* when only the Cartesian coordinates are exchanged leaving the spin coordinates unchanged."



$$\Psi = \psi_e \cdot \psi_v \cdot \psi_r \cdot \psi_I$$

Energy	1	κ^2	κ^4	$\alpha^2\kappa^8$
	1	10^{-2}	10^{-4}	10^{-12}
Mixing	1	10^{-2}	10^{-2}	10^{-8}

Nuclear spin interactions $I{\cdot}I$ $I{\cdot}J$

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$$\left[D_{1/2}\right]^2 = D_1 \oplus D_0$$

The principle of superposition of states

H_2	$\left[D_{1/2}\right]^2 = D_1 \oplus D_0$
H_3^+	$\left[D_{1/2}\right]^3 = D_{3/2} \oplus 2D_{1/2}$
CH_4	$\left[D_{1/2}\right]^4 = D_2 \oplus 3D_1 \oplus 2D_0$
CH_5^+	$\left[D_{1/2}\right]^5 = D_{5/2} \oplus 4D_{3/2} \oplus 5D_{1/2}$

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Polyatomic molecules

Nuclear Spin State Equilibration through Nonmagnetic Collisions*

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

J. Chem. Phys. 46, 3220 (1967)

H_2CO

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

CH_4

$$H_{1b} = (\tfrac{1}{3}A)\{J_x[(I_{1y}+I_{2y}-I_{3y}-I_{4y})+(I_{1z}-I_{2z}-I_{3z}+I_{4z})]$$
$$+J_y[(I_{1z}+I_{2z}-I_{3z}-I_{4z})+(I_{1x}-I_{2x}+I_{3x}-I_{4x})]+J_z[(I_{1x}-I_{2x}-I_{3x}+I_{4x})+(I_{1y}-I_{2y}+I_{3y}-I_{4y})]\}$$

$$H_{2a} = \tfrac{1}{2}B\{[(I_{1z}I_{2z}+\epsilon I_{1x}I_{2x}+\epsilon^* I_{1y}I_{2y})+(I_{1z}I_{2z}+\epsilon^* I_{1x}I_{2x}+\epsilon I_{1y}I_{2y})]$$
$$+[\epsilon^*(I_{1z}I_{3z}+\epsilon I_{1x}I_{3x}+\epsilon^* I_{1y}I_{3y})+\epsilon(I_{1z}I_{3z}+\epsilon^* I_{1x}I_{3x}+\epsilon I_{1y}I_{3y})]$$
$$+[\epsilon(I_{1z}I_{4z}+\epsilon I_{1x}I_{4x}+\epsilon^* I_{1y}I_{4y})+\epsilon^*(I_{1z}I_{4z}+\epsilon^* I_{1x}I_{4x}+\epsilon I_{1y}I_{4y})]$$
$$+[\epsilon(I_{2z}I_{3z}+\epsilon I_{2x}I_{3x}+\epsilon^* I_{2y}I_{3y})+\epsilon^*(I_{2z}I_{3z}+\epsilon^* I_{2x}I_{3x}+\epsilon I_{2y}I_{3y})]$$
$$+[\epsilon^*(I_{2z}I_{4z}+\epsilon I_{2x}I_{4x}+\epsilon^* I_{2y}I_{4y})+\epsilon(I_{2z}I_{4z}+\epsilon^* I_{2x}I_{4x}+\epsilon I_{2y}I_{4y})]$$
$$+[(I_{3z}I_{4z}+\epsilon I_{3x}I_{4x}+\epsilon^* I_{3y}I_{4y})+(I_{3z}I_{4z}+\epsilon^* I_{3x}I_{3x}+\epsilon I_{3y}I_{4y})]\},$$

$$H_{2b} = -\tfrac{3}{2}B[(I_{1x}I_{2y}+I_{1y}I_{2x}-I_{3x}I_{4y}-I_{3y}I_{4x})+(I_{1y}I_{3z}+I_{1z}I_{3y}-I_{2y}I_{4z}-I_{2z}I_{4y})+(I_{1x}I_{4z}+I_{1z}I_{4x}-I_{2x}I_{3z}-I_{2z}I_{3x})]$$

H_2CO

$$\hat{H}'_{I\cdot J} = M_{XZ}(I_{1X} - I_{2X})J_Z + M_{ZX}(I_{1Z} - I_{2Z})J_X + Tr.$$
$$\hat{H}'_{I\cdot I} = N_{XZ}(I_{1X}I_{2Z} - I_{1Z}I_{2X}) + Tr.$$

NH_3

$$\hat{H}'_{I\cdot J} = M_{XZ}[(2I_{3X} - I_{1X} - I_{2X})J_Z + \sqrt{3}(I_{1Y} - I_{2Y})J_Z]$$
$$+ M_{ZX}[-(2I_{3Z} - I_{1Z} - I_{2Z})J_Y + \sqrt{3}(I_{1Z} - I_{2Z})J$$
$$+ M_{XY}[\{(2I_{3X} - I_{1X} - I_{2X}) - \sqrt{3}(I_{1Y} - I_{2Y})\}J_X$$
$$- \{(2I_{3Y} - I_{1Y} - I_{2Y}) + \sqrt{3}(I_{1X} - I_{2X})\}J_Y] + Tr.$$

$$\hat{H}'_{I\cdot I} = N^{+}_{ZX}[2(I_{1Z}I_{2X} + I_{2Z}I_{1X}) - (I_{1Z} + I_{2Z})I_{3X}$$
$$- I_{3Z}(I_{1X} + I_{2X}) - \sqrt{3}(I_{1Z} - I_{2Z})I_{3Y}$$
$$- \sqrt{3}I_{3Z}(I_{1Y} - I_{2Y})] + N^{-}_{ZX}[2(I_{1Z}I_{2Y} - I_{2Z}I_{1Y})$$
$$+ (I_{1Z} - I_{2Z})I_{3Y} - I_{3Z}(I_{1Y} - I_{1X})$$
$$- \sqrt{3}(I_{1Z} + I_{2Z})I_{3X} + \sqrt{3}I_{3Z}(I_{1X} + I_{2Y})]$$
$$+ N_{XY}[2(I_{1X}I_{2X} - I_{1Y}I_{2Y}) - (I_{2X}I_{3X} + I_{3X}I_{1X}$$
$$- I_{2Y}I_{3Y} - I_{3Y}I_{1Y}) - \sqrt{3}(I_{2X}I_{3Y} - I_{3Y}I_{1X}$$
$$+ I_{2Y}I_{3X} - I_{3X}I_{1Y})] \quad (4$$

Handbook

Applications to interstellar molecules

Ortho↔Para conversion in interstellar space

- Radiative
- Collisional
- Chemical ←

Neutral molecules

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

$$H^+ + o\text{-}H_2CO \rightleftarrows H^+ + p\text{-}H_2CO$$

A. Dalgarno, J. H. Black, J. C. Weisheit ApL, 14, 77 (1973)

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

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

J. Le Bourlot A&A, 242, 235 (1991)

Ions

$$H_2 + o\text{-}H_3^+ \leftrightarrow H_2 + p\text{-}H_3^+$$

$$H_2 + p\text{-}H_2O^+ \rightarrow H + H_3O^+$$

Nuclear spin selection rules

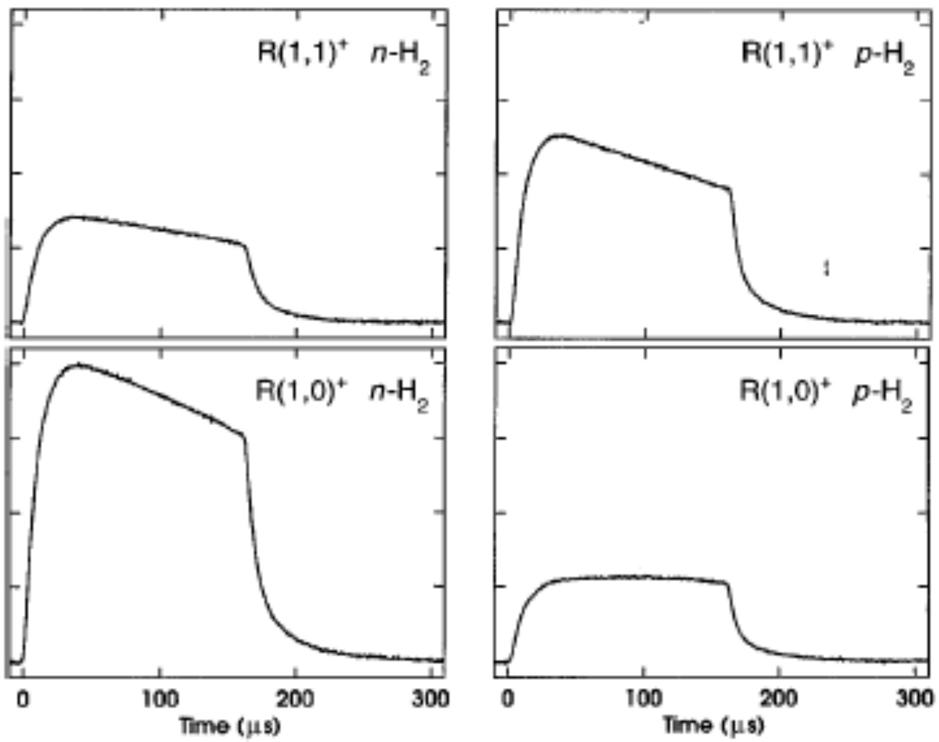
Detailed symmetry selection rules for reactive collisions

by MARTIN QUACK† Mol. Phys. 34, 477 (1977)

$$H_2^+ + H_2 \leftrightarrow (H_4^+)^* \leftrightarrow H + H_3^+ \qquad H_3^+ + H_2 \leftrightarrow (H_5^+)^* \leftrightarrow H_2 + H_3^+$$

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

Dairene Uy,* Michel Cordonnier,† and Takeshi Oka Phys. Rev. Lett. 78, 3844 (1997)



$H_3^+ + H_2 \rightarrow H_3^+ + H_2$

spin species[c]	Weight	*oo*[d]	*op*	*po*	*pp*
oo	12	37/5	1	14/5	4/5
op	4	1	1	2	0
po	12	14/5	2	28/5	8/5
pp	4	4/5	0	8/5	8/5

Proton hop $H_3^+ + \tilde{H}_2 \rightarrow H_2 + \tilde{H}_2H^+$

Proton exchange $H_3^+ + \tilde{H}_2 \rightarrow H_2\tilde{H} + H\tilde{H}$

2.4 : 1

Crabtree, McCall et al. (2011)

Nuclear spin selection rules in chemical reactions by angular momentum algebra

Takeshi Oka* J. Mol. Spectrosc. 228, 635 (2004)

Quack Permutation inversion group (Molecular symmetry group)

C_{2v}, C_{3v}, D_{2d}, D_{3h}, T_d, ……
E, C_2, C_3, σ_v, σ_h, I, ……
A_1, A_2, B_1, B_2, A', A'', E, F, …..

$$\Psi = \psi_{\text{coordinate}} \cdot \boxed{\psi_{\text{spin}}}$$

Frobenius' reciprocity
G. Frobenius Sitzber. Preuss. Akad. 501 (1898)
J. K. G. Watson, Can. J. Phys. 43, 1996 (1965)

Rotation group D_I

$$D_{I_1} \otimes D_{I_2} = D_{I_1+I_2} \oplus D_{I_1+I_2-1} \oplus \cdots\cdots \oplus D_{|I_1-I_2|}$$

The Almighty Formula

H_2 $\left[D_{1/2}\right]^2 = D_1 \oplus D_0$

H_3^+ $\left[D_{1/2}\right]^3 = D_{3/2} \oplus 2D_{1/2}$

CH_4 $\left[D_{1/2}\right]^4 = D_2 \oplus 3D_1 \oplus 2D_0$

CH_5^+ $\left[D_{1/2}\right]^5 = D_{5/2} \oplus 4D_{3/2} \oplus 5D_{1/2}$

Advantages

Simplicity
Any value of *n*
Any value of spin
Discriminating reactions

Microcanonical statistical study of ortho-para conversion in the reaction $H_3^+ + H_2 \rightarrow (H_5^+)^* \rightarrow H_3^+ + H_2$ at very low energies

Kisam Park and John C. Light J. Chem. Phys. 126, 044305 (2007)

Ortho ↔ para spontaneous emission in open shell molecules

Closed shell (non-magnetic) molecules	$I{\cdot}I$ $I{\cdot}J$	$\kappa^8\alpha^2 \sim 10^{-12}$	10^{10} years
Open shell (paramagnetic) molecules	$S{\cdot}I$	$\kappa^4\alpha^2 \sim 10^{-8}$	10^2 years

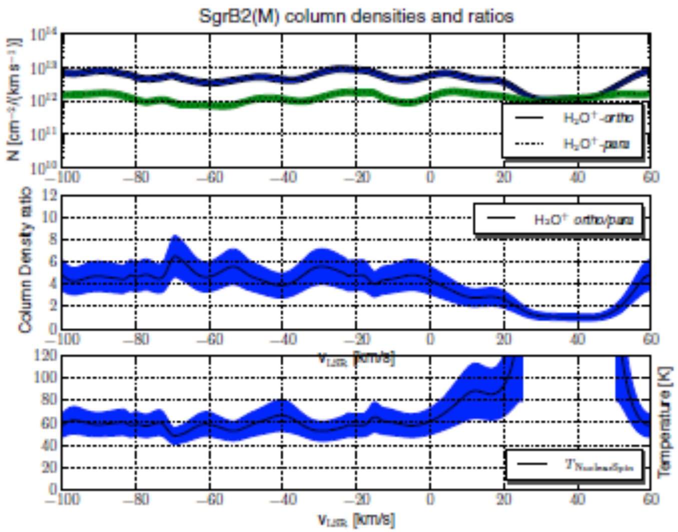
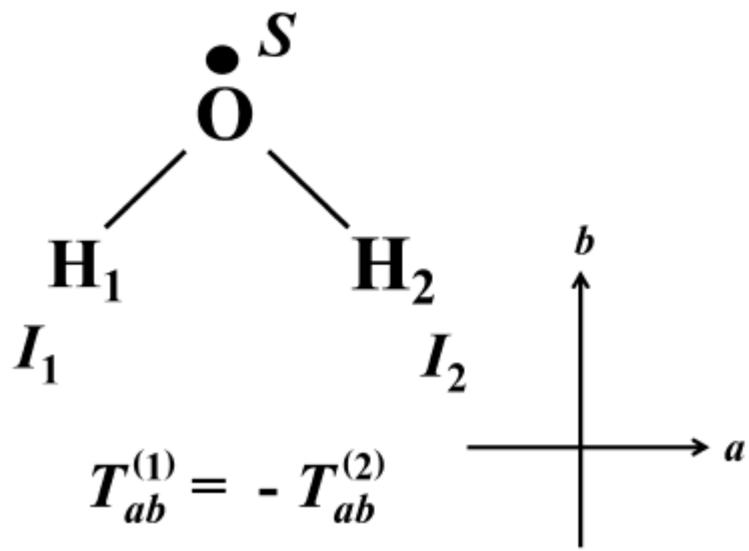


Fig. 3. Column density distribution of *ortho*-H_2O^+ and *para*-H_2O^+ (*upper panel*), o/p ratio (*central panel*) and $T_{nuclearspin}$ distribution (*lower panel*).



$$T_{ab}^{(1)} = - T_{ab}^{(2)}$$

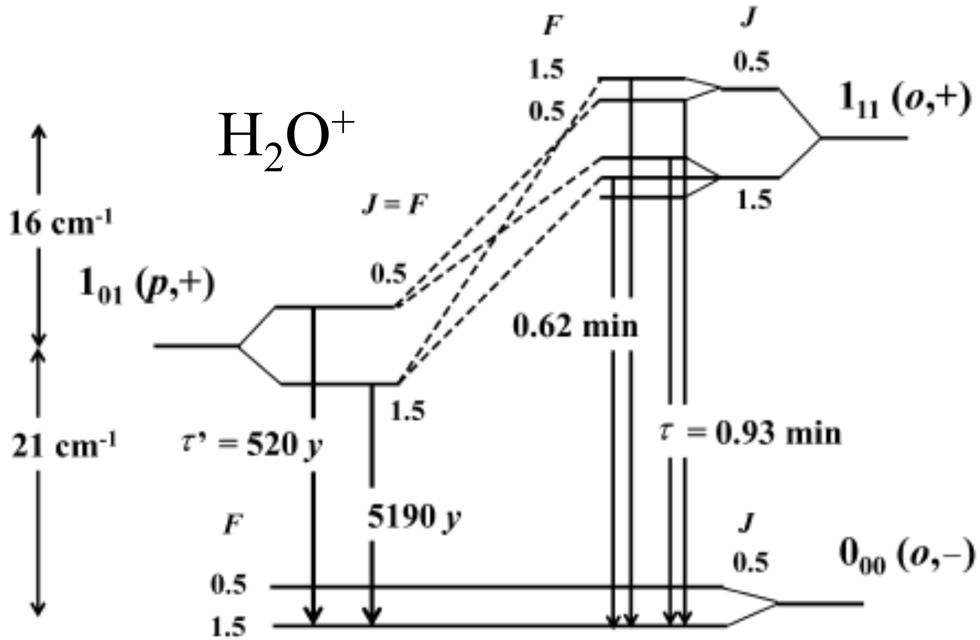
P. Schilke et al. A&A 521, L11 (2010)

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

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

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

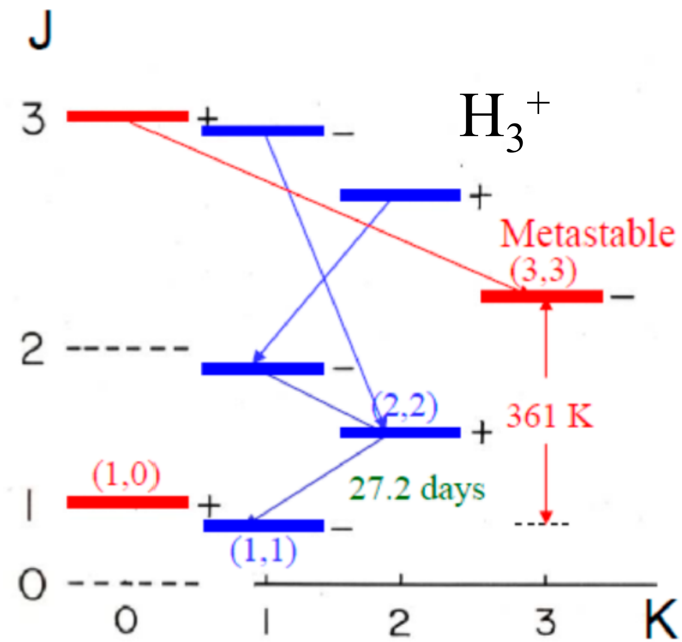
520 years



$$\langle N', K_a', S, J', I', F, M_F | H_1 | N, K_a, S, J, I, F, M_F\rangle = -(-1)^{I'+F+J}(30S(S+1)(2S+1)(2N+1) \times (2N'+1)(2J+1)(2J'+1))^{1/2} \times \langle I' \| \Delta I^{(1)} \| I\rangle \begin{Bmatrix} J' & I' & F \\ I & J & 1\end{Bmatrix} \begin{Bmatrix} N' & S & J' \\ N & S & J \\ 2 & 1 & 1\end{Bmatrix} \times \sum_{p=\pm1} (-1)^{N'-K_a'} \begin{pmatrix} N' & 2 & N \\ -K_a' & p & K_a\end{pmatrix} T_p^{(2)}$$

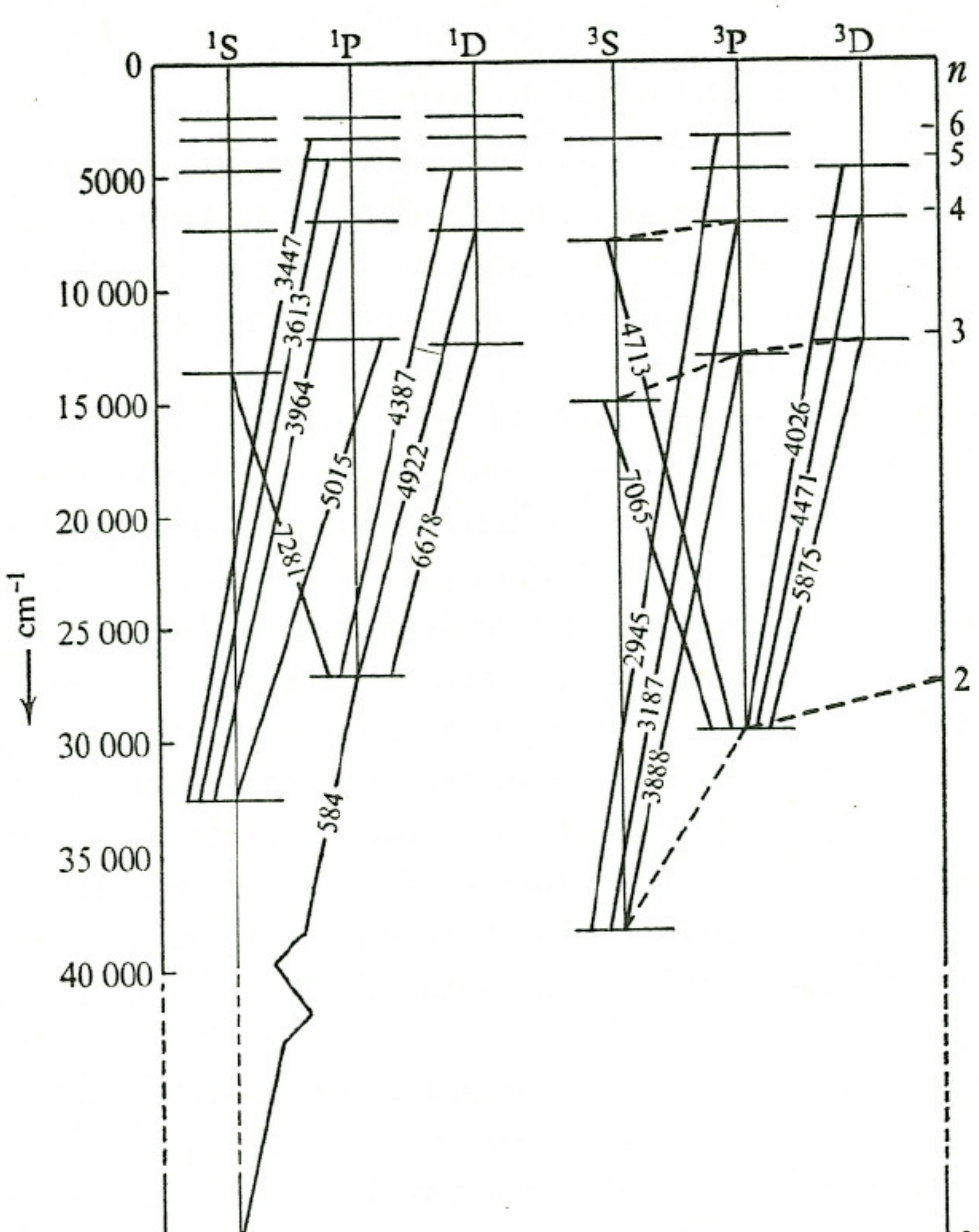
NH_3 CALCULATED TIME FOR SPONTANEOUS EMISSION t AND ABSORPTION COEFFICIENT γ AT ROOM TEMPERATURE

Transition	ν(cm^{-1})	t(10^9 sec)	γ(10^{-7} cm^{-1})*
(2,2)→(1,1)	28.53	7.32	0.06
(3,3)→(2,0)	25.93	1.37	0.9
(4,4)→(3,1)	23.36	0.69	0.9
(5,5)→(4,2)	20.80	0.50	1.2
(6,6)→(5,3)	18.25	0.44	2.4

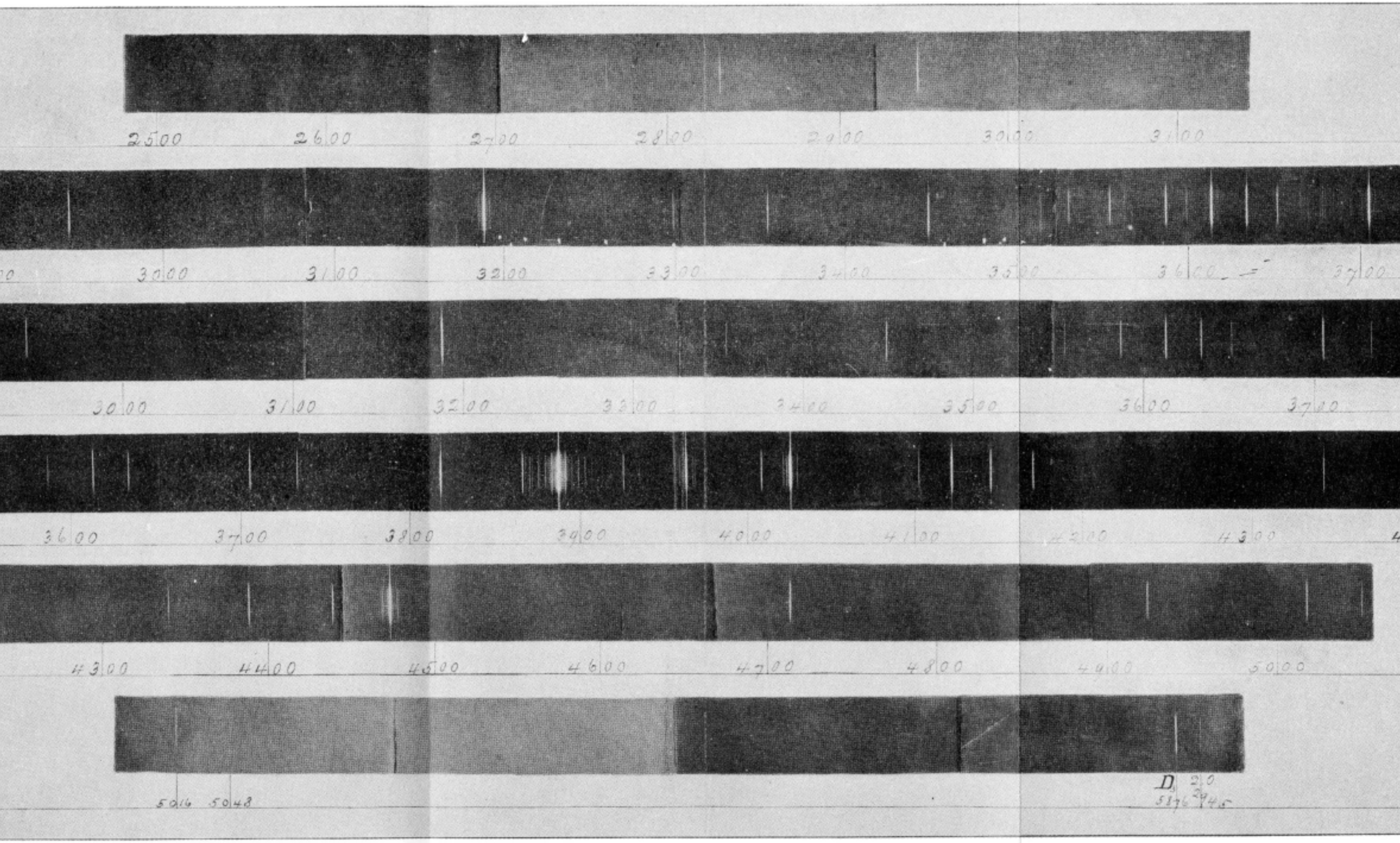


Oka, Shimizu, Shimizu, Watson ApJ, 165, L15 (1971)

Oka, Geballe, Goto, Usuda, McCall ApJ, 632, 882 (2005)



^1S
^1P
^1D
^3S
^3P
^3D
n
0
5000
10 000
15 000
20 000
25 000
30 000
35 000
40 000
cm^{-1}
6
5
4
3
2
3447
3613
3964
5015
4387
4922
6678
7281
584
4713
7065
2945
3187
3888
4026
4471
5875



PHOTOGRAPH OF THE SPECTRUM OF CLÈVEITE GAS TAKEN IN THE FIRST ORDER OF A LARGE ROWLAND CONCAVE GRATING.

There are some impurities visible, principally hydrogen and traces of the cyanogen band 3883 and of nitrogen bands. The strong lines are accompanied by "ghosts" on either side. Two photographs are given of the region from λ2900 to λ3700.