Observation of $\Omega = 1/2$ states in NiH through collisionally induced fluorescence.

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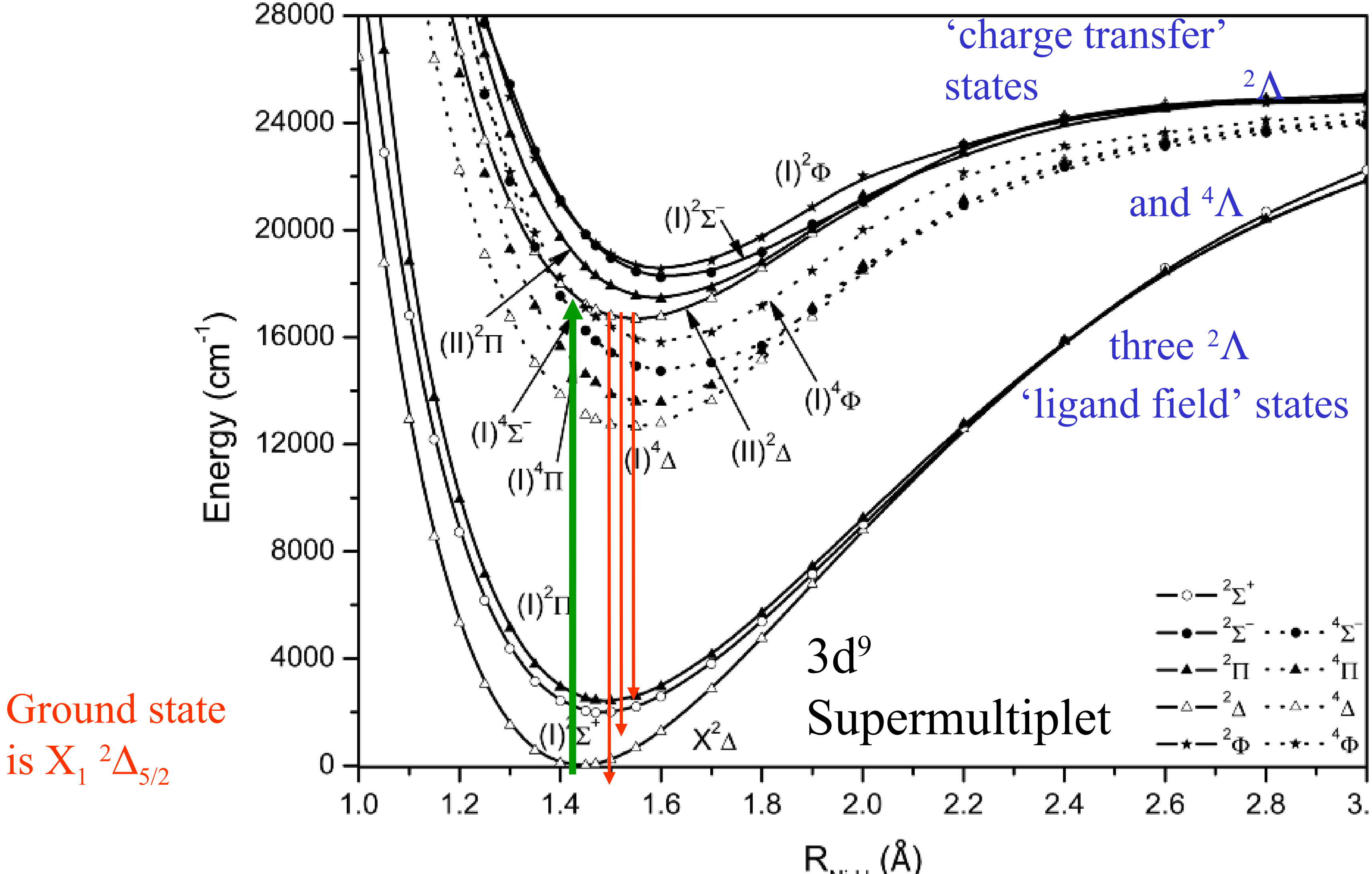
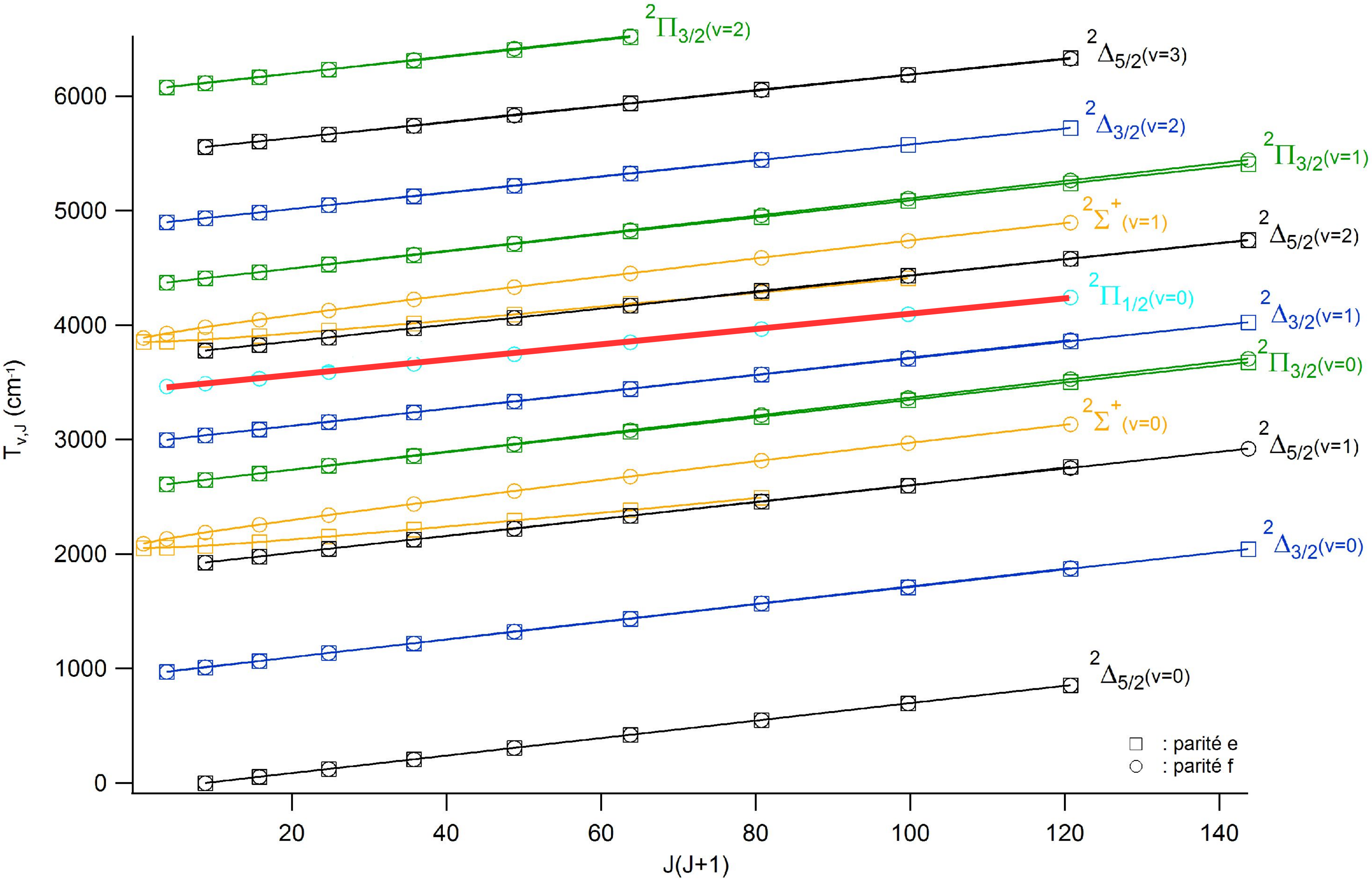
Electronic spectra of NiH



NiH Λ-S potential curves, from Liu & Zou
[J Comp Chem 29 2286 (2007), figure 1].

Overview of $3d^9$ supermultiplet NiH energy levels. No e parity levels observed for $^2\Pi_{1/2}$



The $\Omega = ½$ states are hard to observe because …

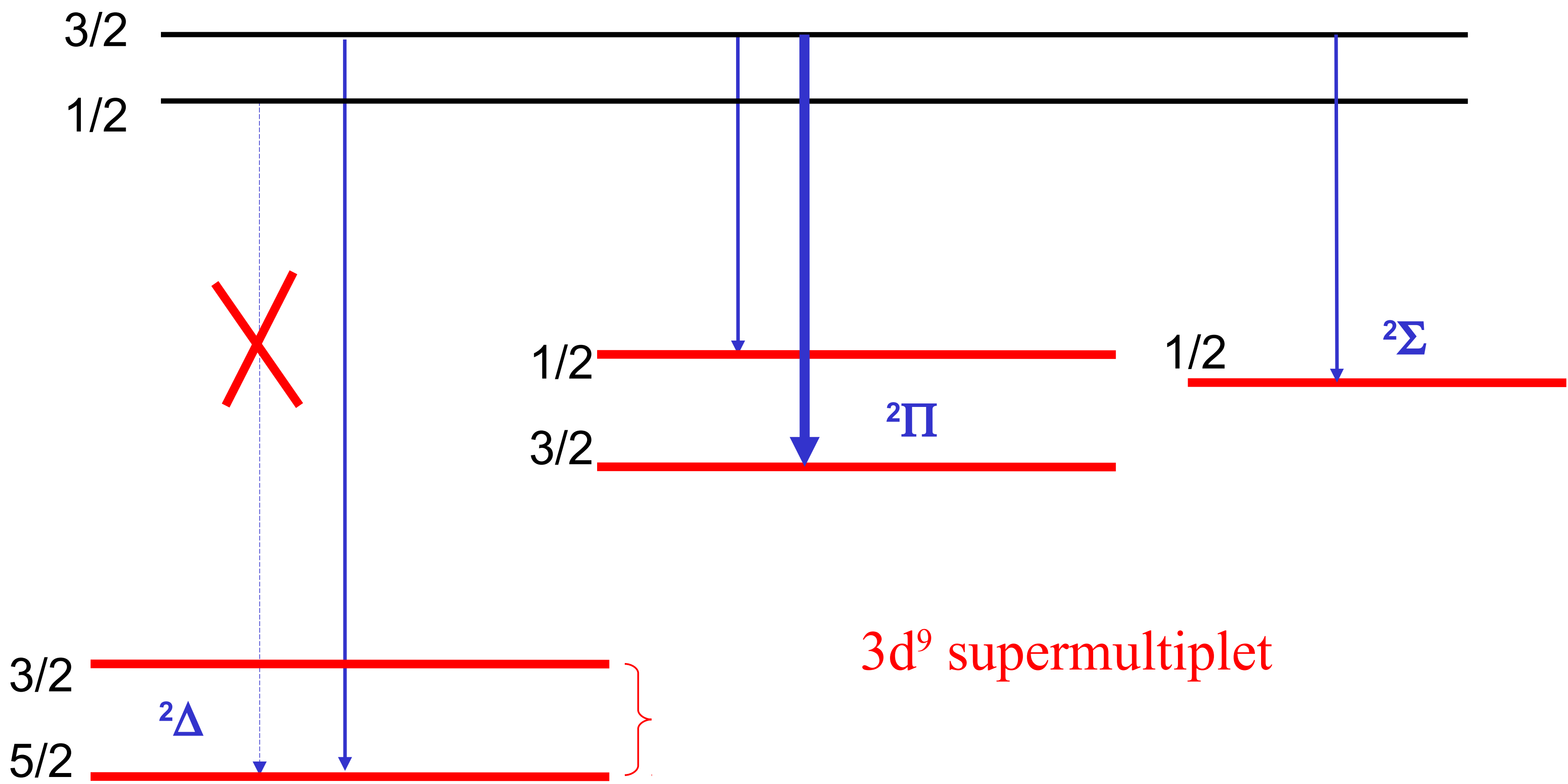
The only electronic state populated in our hollow cathode discharge source is $^2\Delta_{5/2}$ (v=0).

So far, no evidence of direct excitation of $\Omega = ½$ states

Most optical transitions with $\Delta\Omega \neq 0$ are rather weak.
Normal laser excitation + fluorescence to $\Omega'' = ½$ states involves two relatively weak transitions.

Very weak direct fluorescence from I ($\Omega' = 3/2$) has been recorded to v = 0 and v=1 of the low-lying $^2\Sigma^+$ state, and to a few rotational levels of $^2\Pi_{½}$ (v=0 and f parity only)

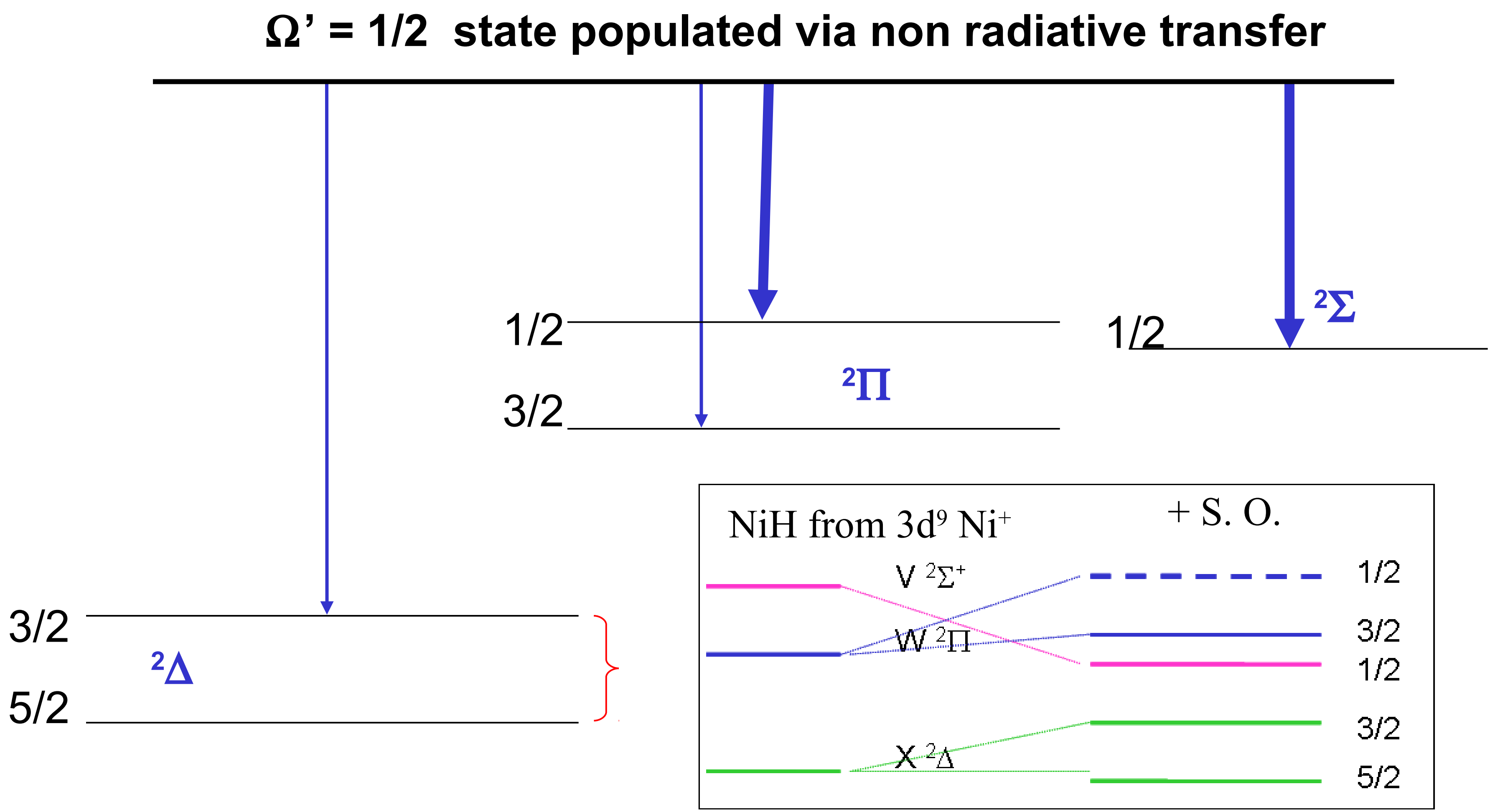
The Ω = ½ states are hard to observe because …



v''=0 Most optical transitions with $\Delta\Omega \neq 0$ are rather weak.

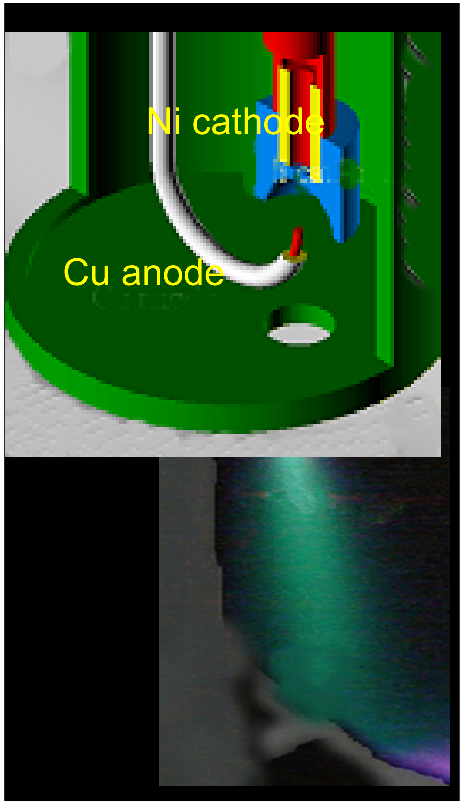
The $^2\Sigma$, $^2\Pi$, $^2\Delta$ lower states are HEAVILY mixed by spin-orbit interactions

Solution ? Populate an Ω'=½ excited state through collision and record fluorescence



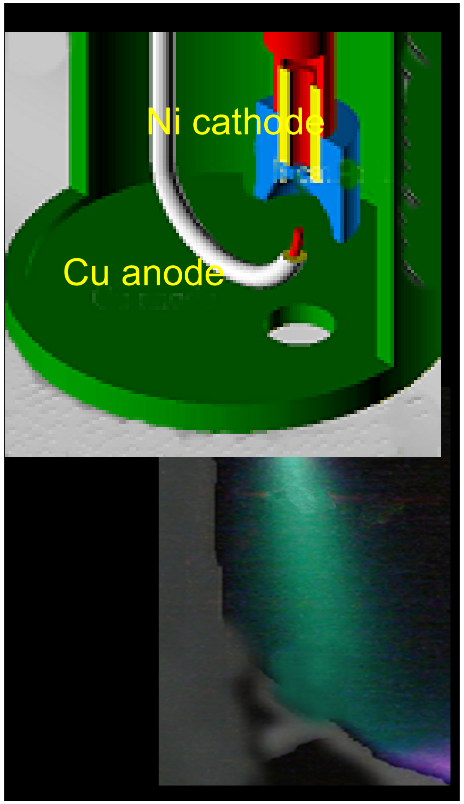
The $^2\Sigma$, $^2\Pi$, $^2\Delta$ lower states are HEAVILY mixed by spin-orbit interactions

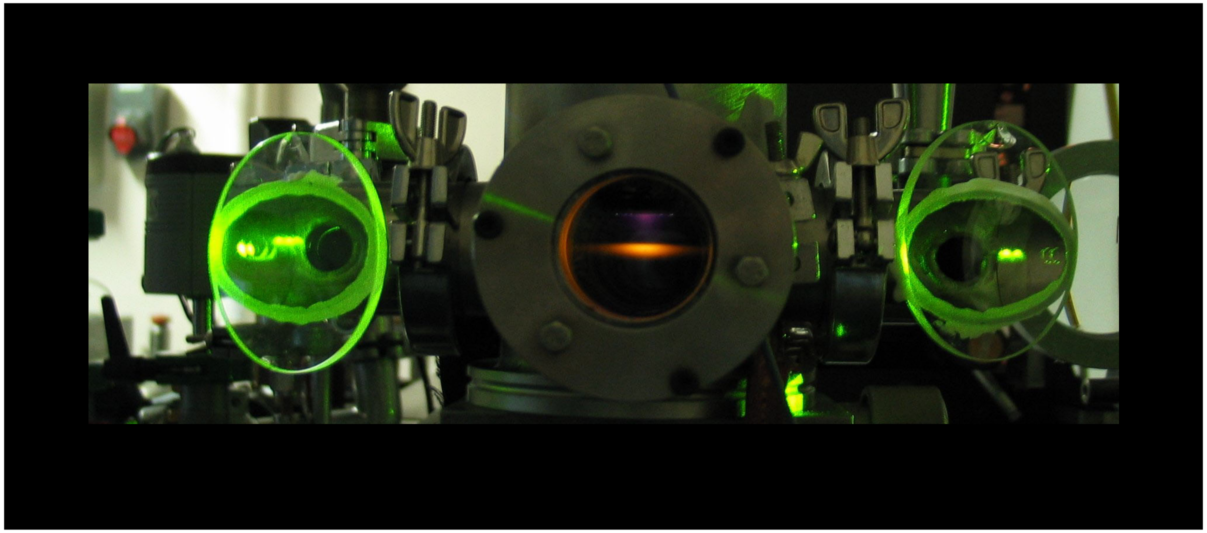
NiH is produced in a hollow cathode discharge source, I = 100-200 mA, p 1-2 Torr of a 10% H_2/Ar mixture



Laser excitation ~ 1 cm downstream from the cathode

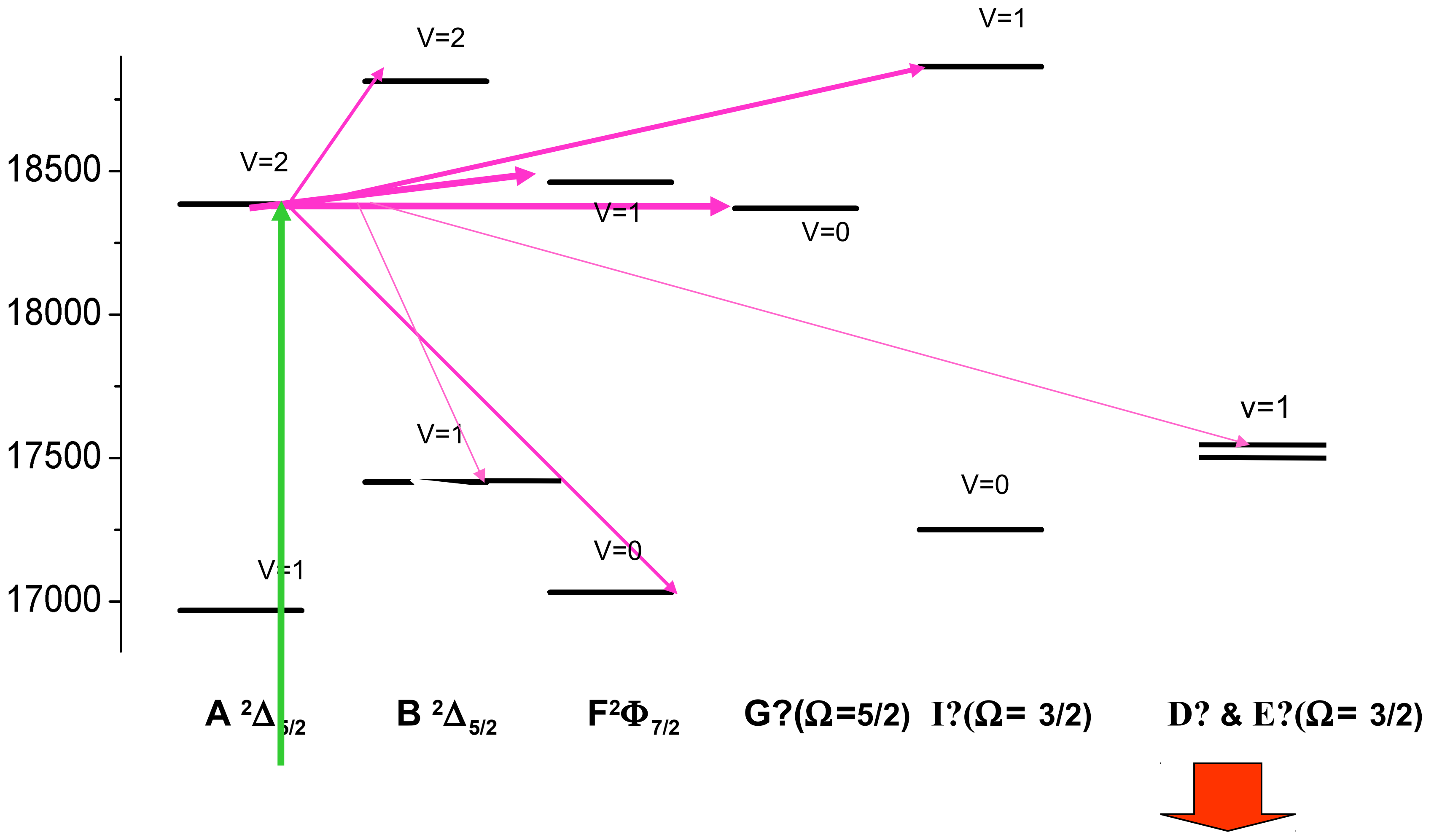
NiH is produced in a hollow cathode discharge source, I = 100-200 mA, p 1-2 Torr of a 10% H_2/Ar mixture





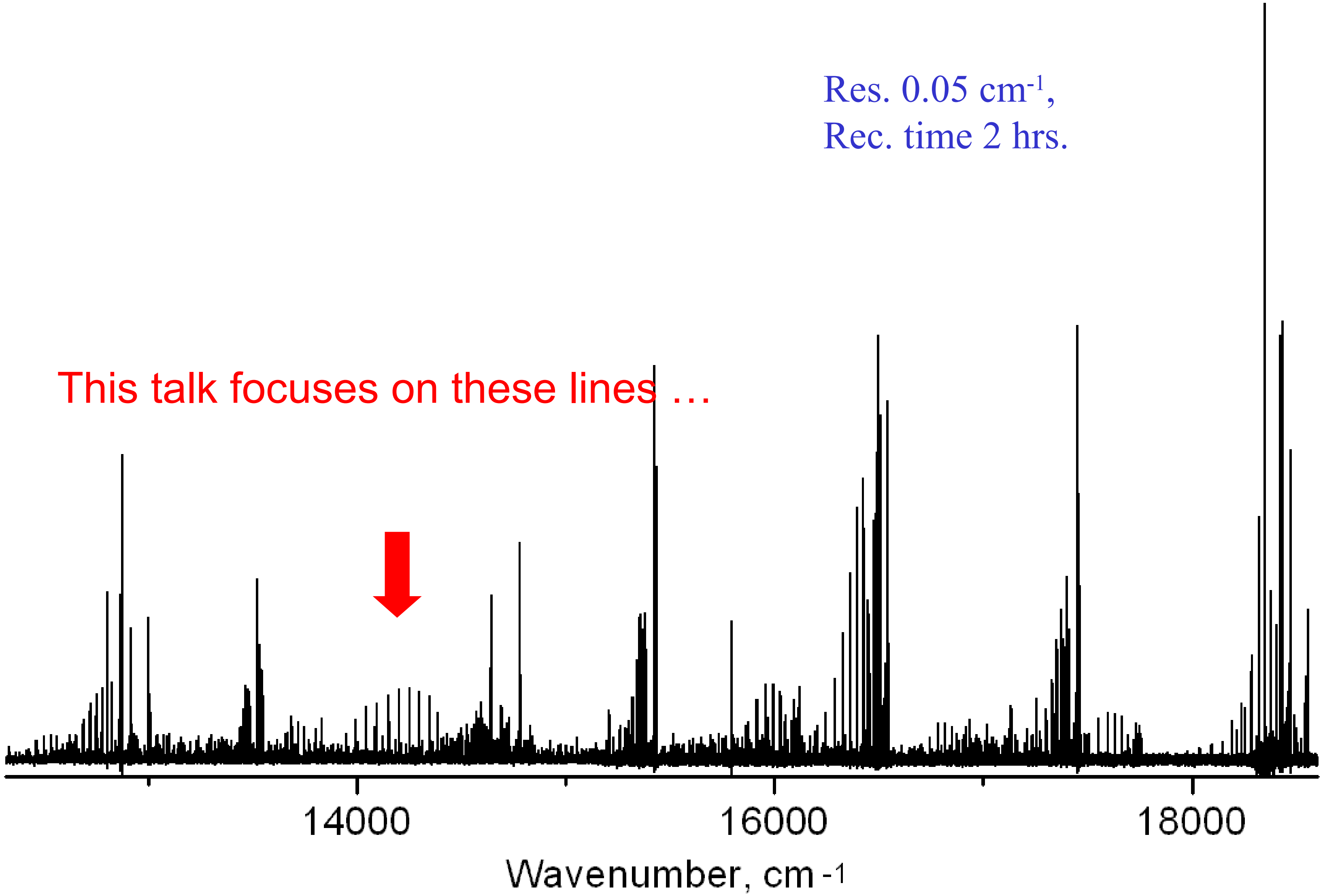
Bright fluorescence is clearly visible by eye, and is transferred to FTS.

States populated in NiH after excitation of v=2, A [5/2]



Observe fluorescence from all of these to <u>three</u> low-lying, very heavily mixed, $^2\Lambda$ states.

Collisionally induced fluorescence following selective laser excitation of J'=2½ , v'=2, A(Ω=5/2) ^{58}NiH



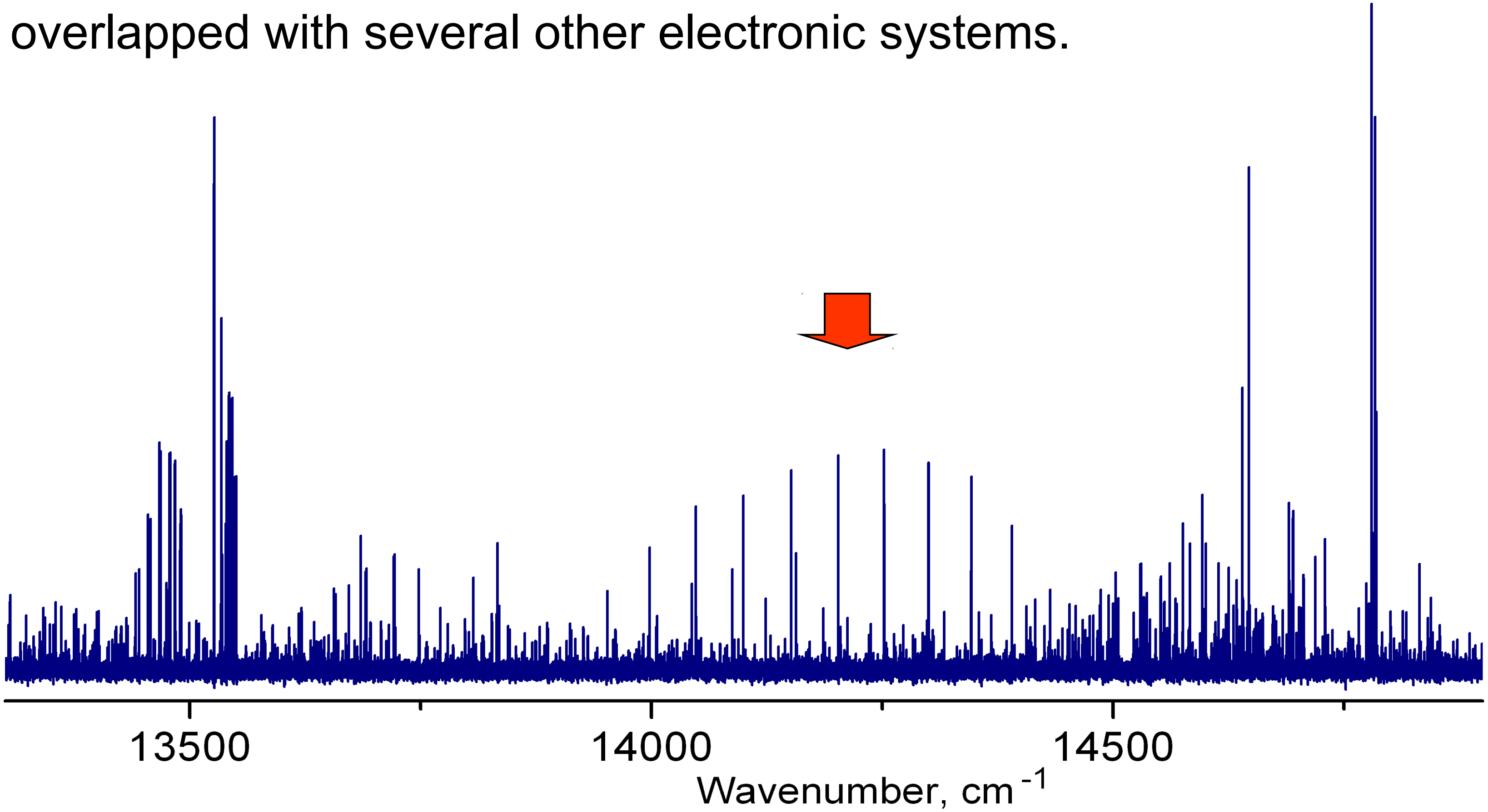
BUT we can not easily assign the ‘new’ transition seen in collisionally induced fluorescence.

Seems to have only one branch

Has no resolved Λ doubling (unlike all other states analysed so far)

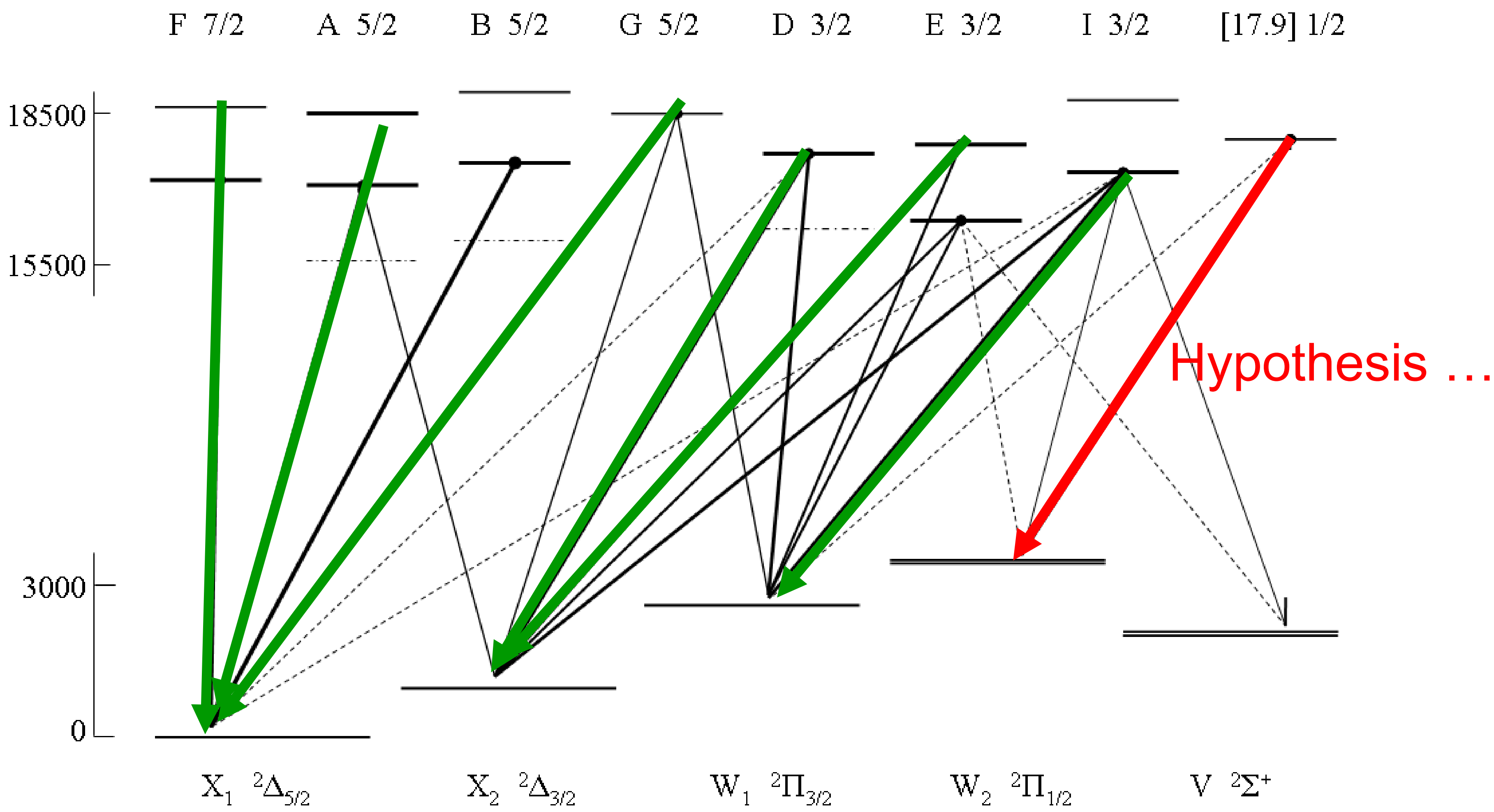
Can not find ANY recognizable combination differences

It is overlapped with several other electronic systems.



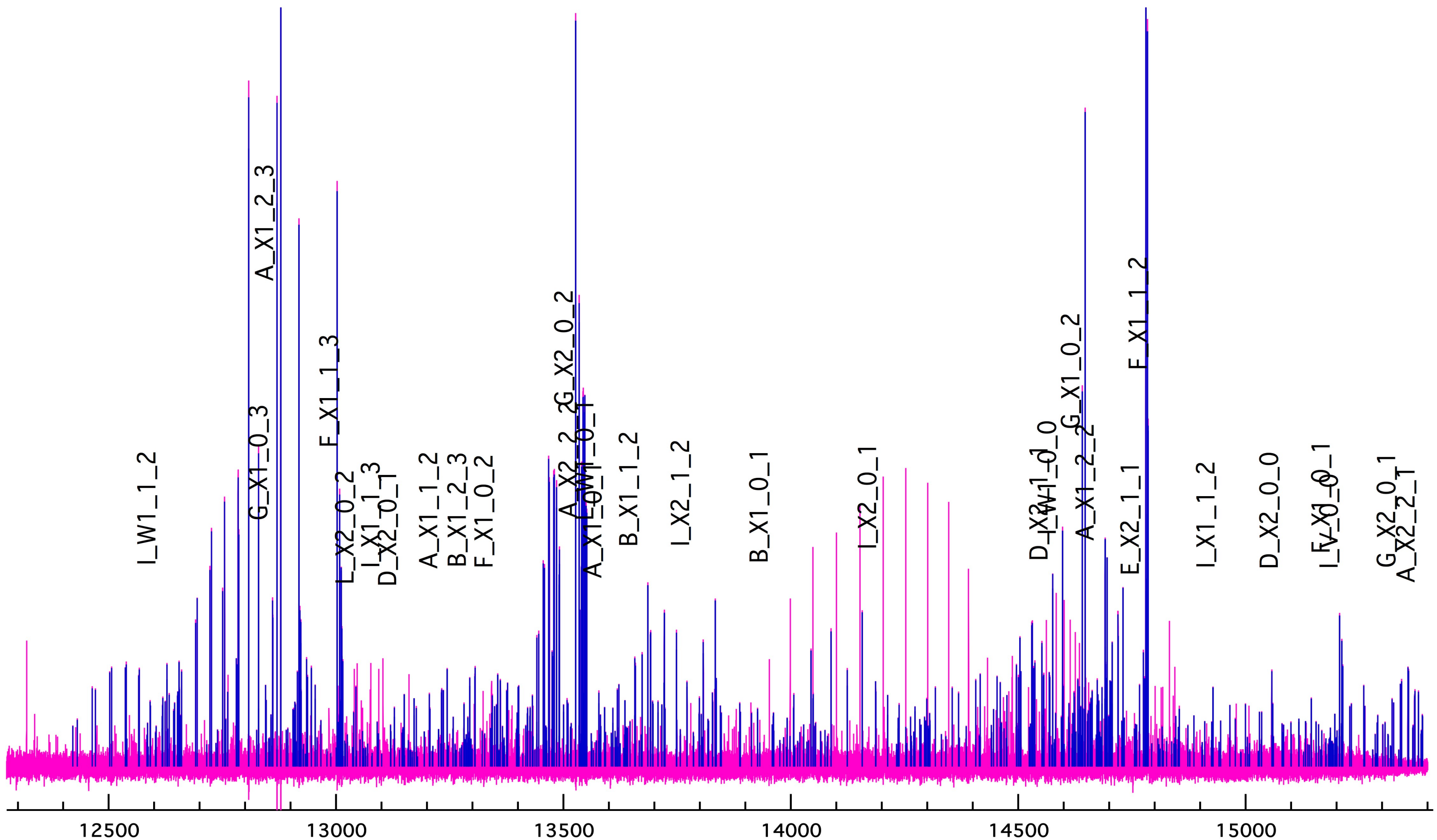
In the same energy region …

… a selection of A-X, D-X, E-X, G-X, F-X and I-W bands !



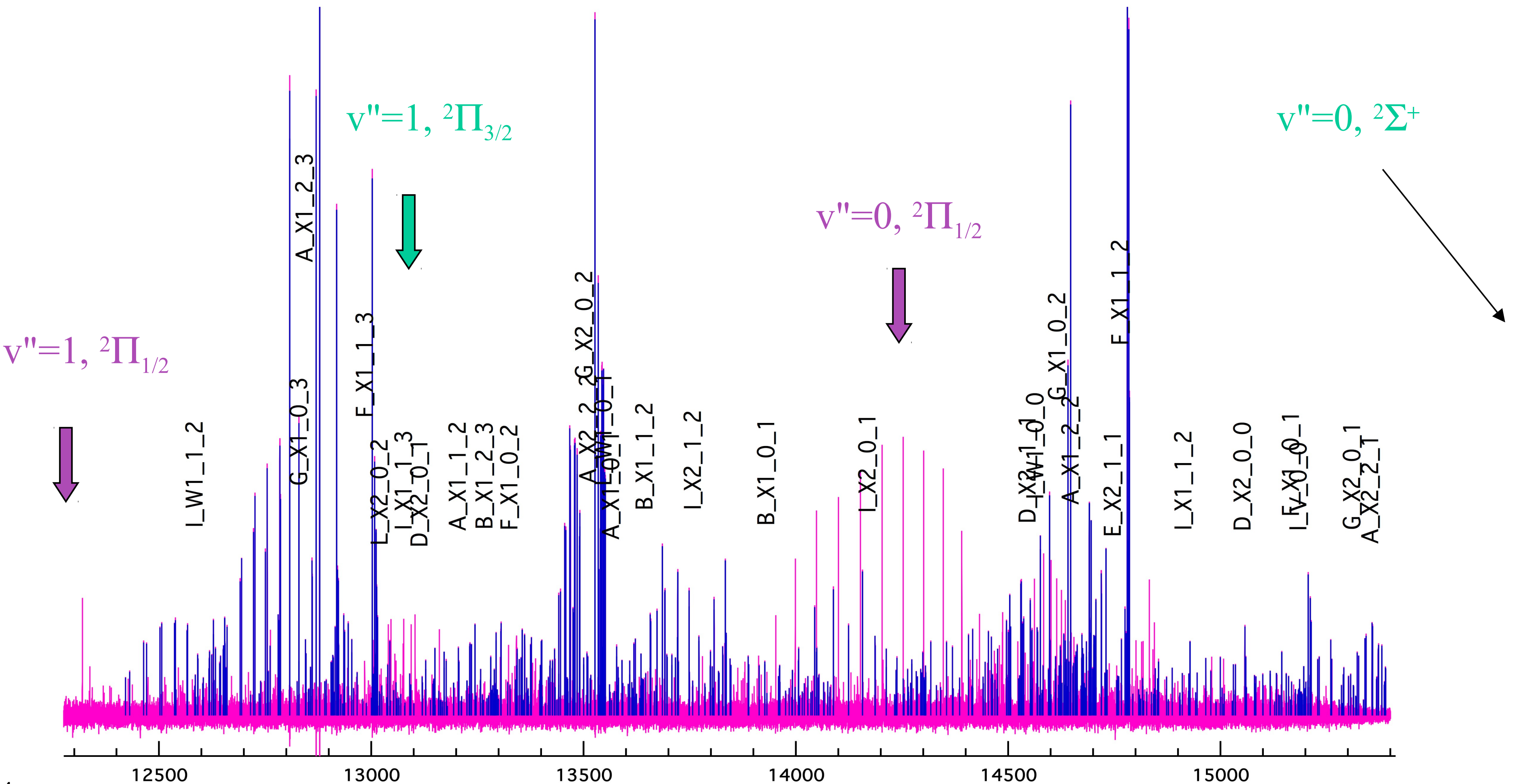
Eliminate all transitions we can predict between known states. *(Igor Pro routine (DWT))* Then look at the spectrum again.

In magenta : all lines.   In blue : assigned lines.



Then look at the spectrum even harder. We finally recognized combination differences between ${}^2\Sigma^+$ and ${}^2\Pi_{3/2}$

PROGRESS : Assigned transitions to give secure ΔF' … and J numbering in the upper state ☺



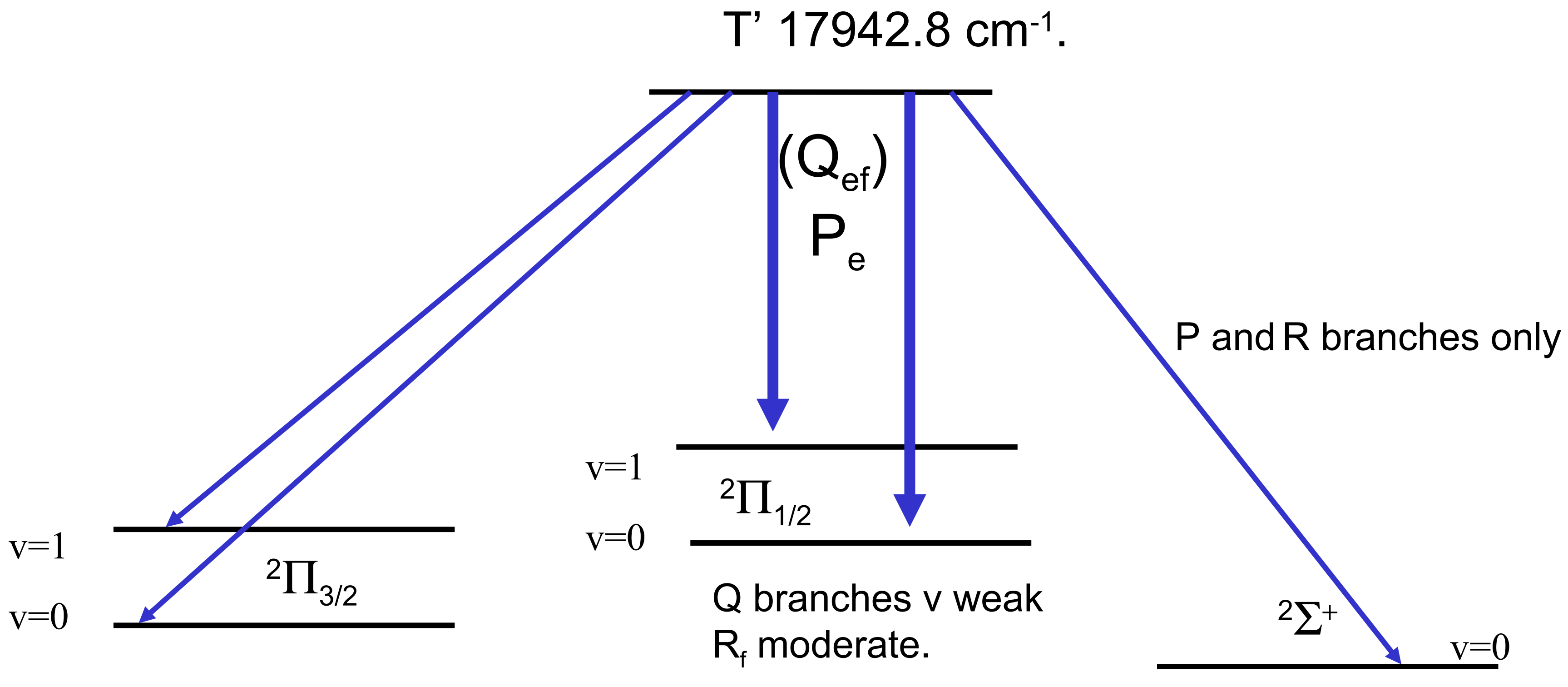
Having found (weak) transitions to known lower states …

J' numbering comes from V $^2\Sigma^+$ -W_1 $^2\Pi_{3/2}$ combination differences.

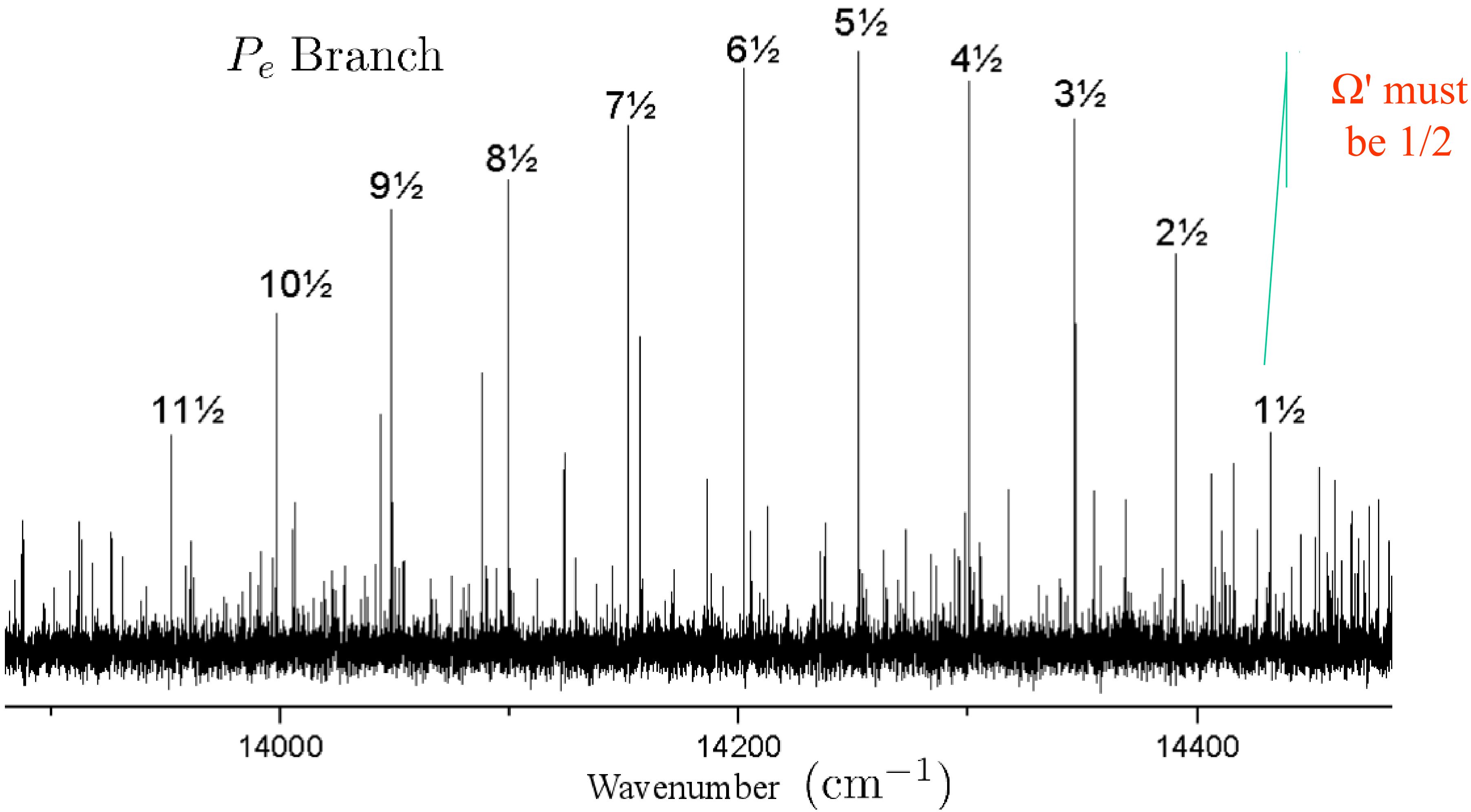
Upper state energies come from T''_{vJ} in V $^2\Sigma^+$ and W_1 $^2\Pi_{3/2}$.

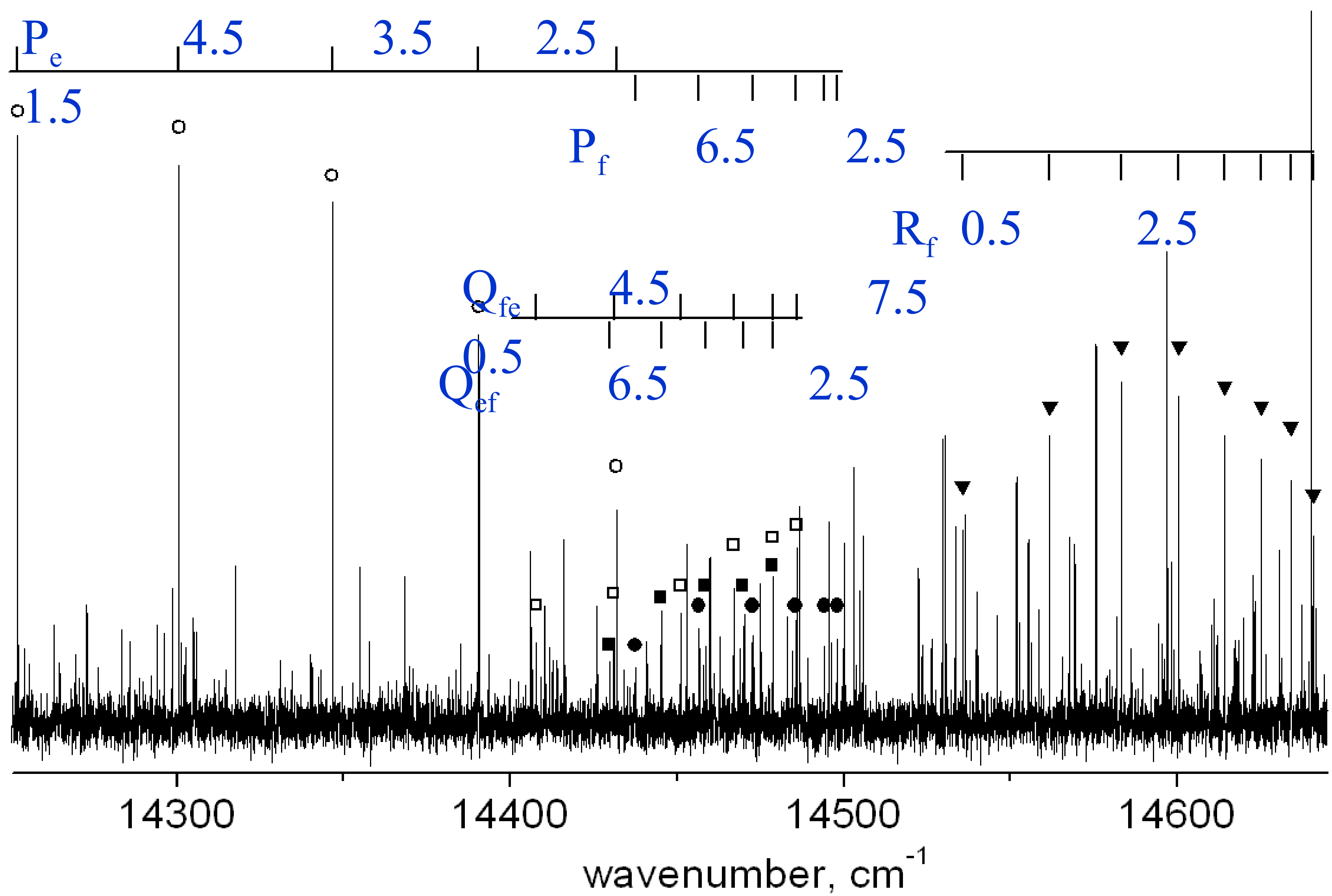
T'(J=0.5 e) 17942.84 cm^{-1},

T'(J=0.5 f) 17962.98 cm^{-1}.



Quantum numbers !
Laser excited J'=2½ , v'=2, A(Ω=5/2) ^{58}NiH



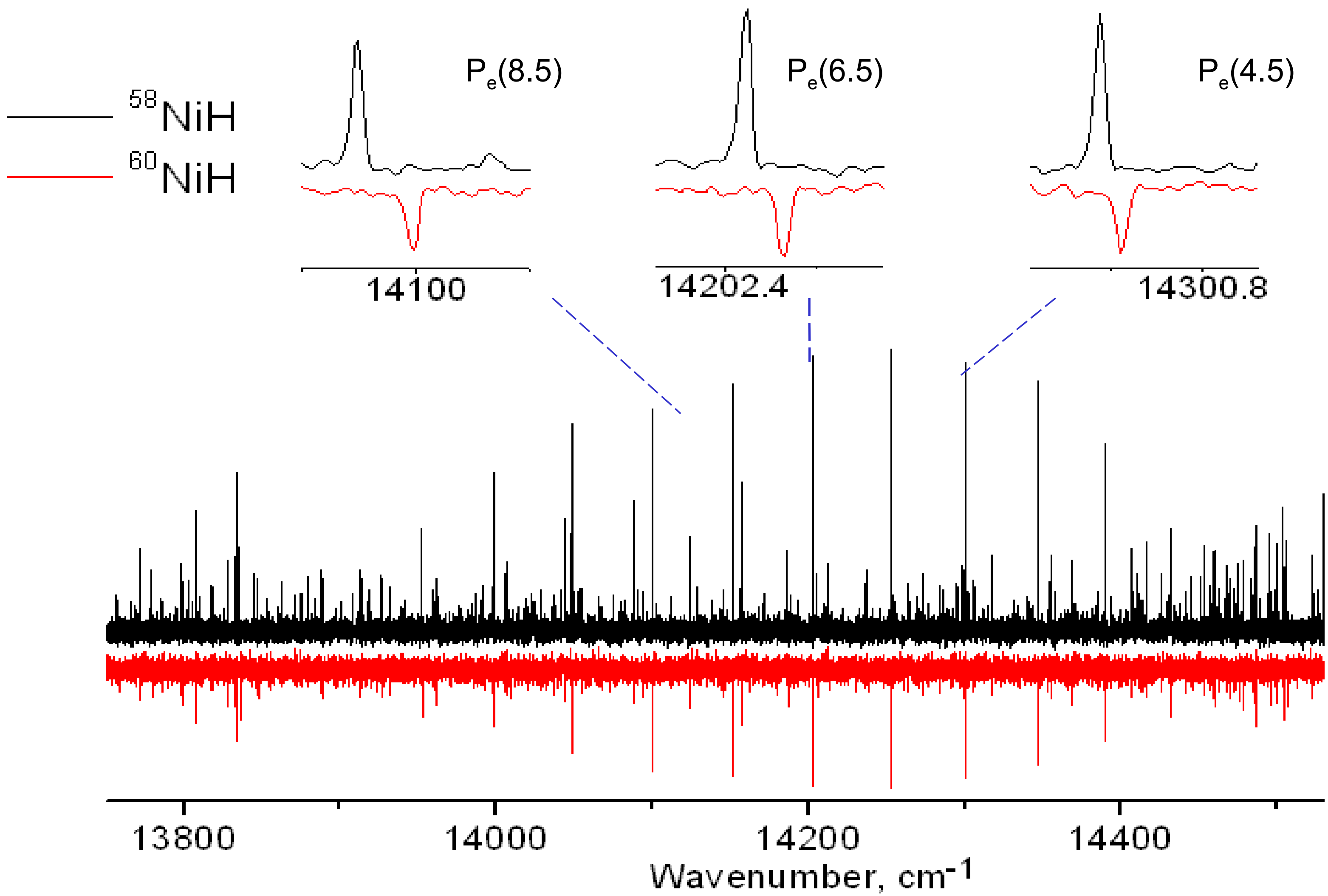


Pe
4.5
3.5
2.5
1.5
Pf
6.5
2.5
Rf
0.5
2.5
Qfe
4.5
7.5
0.5
Qef
6.5
2.5
14300
14400
14500
14600
wavenumber, cm-1

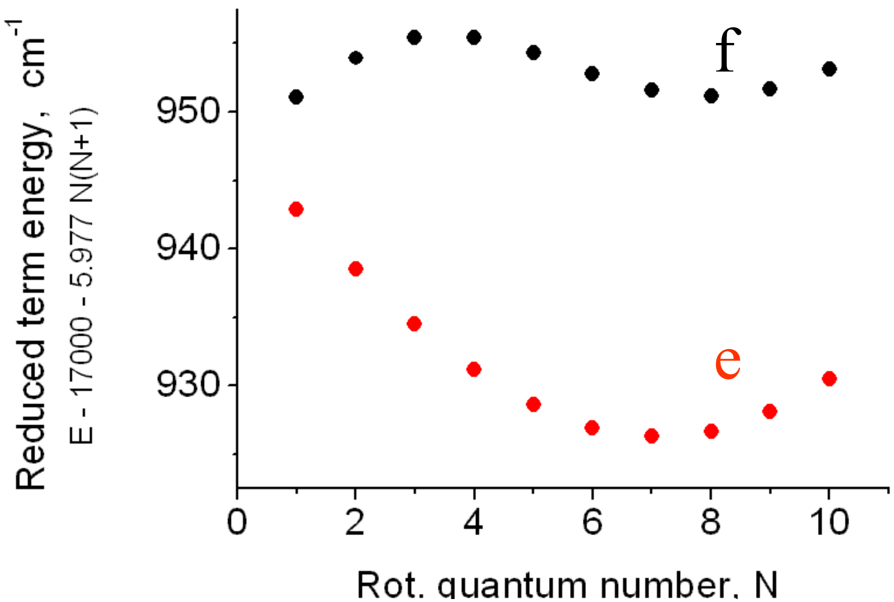
What can we say about the upper state, [0.5]17.9 ?

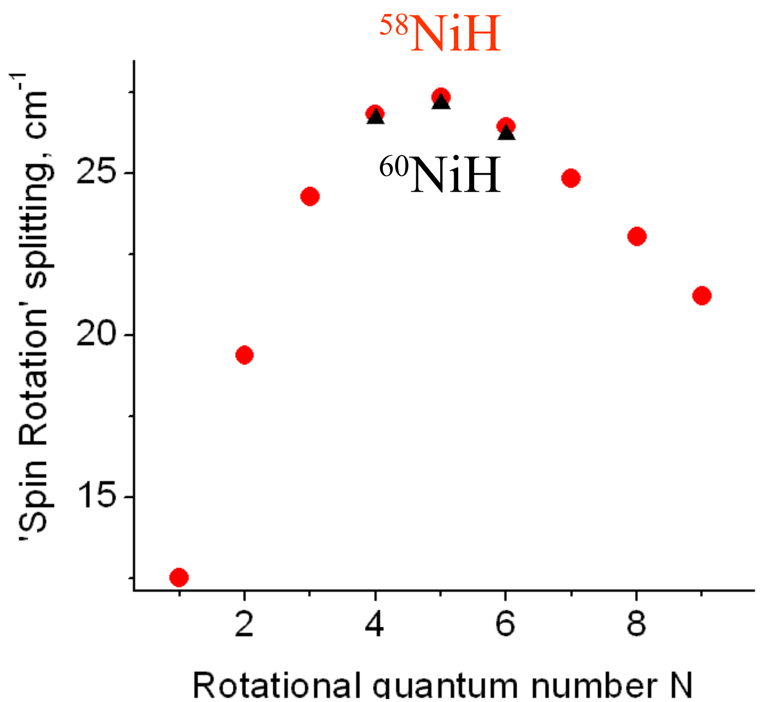
v' = 0 as there is no isotope shift in the strong transitions to v" =0 W_2 $^2\Pi_{1/2}$

Isotope shifts ~ 0.2 cm^{-1} for P(7½) → ~ 0.01 cm^{-1} for P_e(1½)



It has unusual spin-rotation splittings





<u>Parameters for ^{58}NiH</u>.

T_0 = 17945.3(7) cm^{-1},

B_0 = 5.75(4) cm^{-1}

D_0 = -2.3(3) x 10^{-6} cm^{-1}

γ_0 = -6.6(3) cm^{-1}

Yet another 'irregular' electronic state in NiH : can we identifiy it ?
The parameters are not well defined, but do allow comparison with ab initio results

Upper state is the Ω=1/2 component of a $^2\Pi$ state

Final assignment of the new upper electronic state comes from comparison with ab initio calculations of the Ω states of NiH.

Extract from Zou and Liu [J Comp Chem **29** 2286 (2007)].

State(Ω)	T_e	R_0(Å)	Components at R_e
6(1/2)	15733	1.619	76% $^4\Sigma^-$ + 22 % $^4\Pi$
7(1/2)	**17821**	**1.638**	**72 % $^2\Pi$ + 25 % $^2\Sigma^-$**
8(1/2)	19151	1.650	26% $^2\Pi$ + 72% $^2\Sigma^-$

7(1/2) state preferred over 8(1/2) on the grounds of energy match, and reasonably strong transitions to 1 $^2\Sigma^+$ and 1 $^2\Pi_{1/2}$

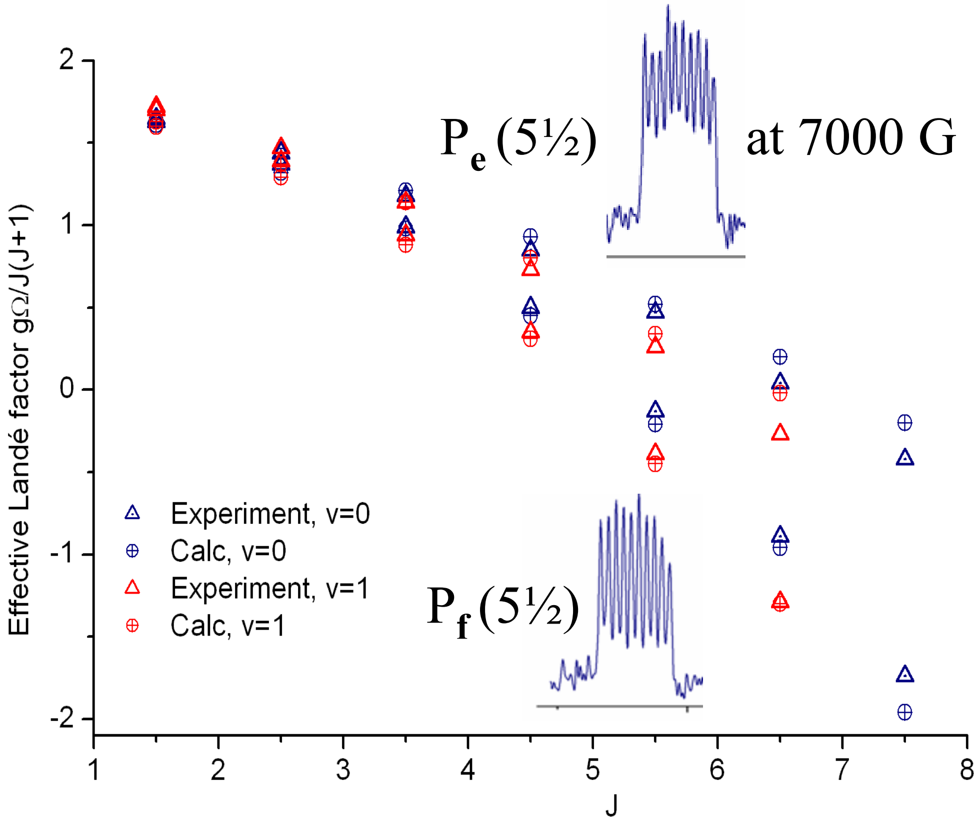
Experimentally, we have T_0 = 17945.3(7) cm^{-1} and R_0 = 1.72 Å

Extended observations of the (1) $^2\Pi_{1/2(e,f)}$ state

The low-lying ro-vibrational levels of the 'supermultiplet' states $E < 5000$ cm^{-1} have all been located (e and f parity, $J < 9.5$)

An improved fit to a full energy matrix Gray has been performed.

Parameters from our new fit reproduce observed Landé factors from Zeeman spectra better than before.



Comments, Conclusions and Acknowledgements

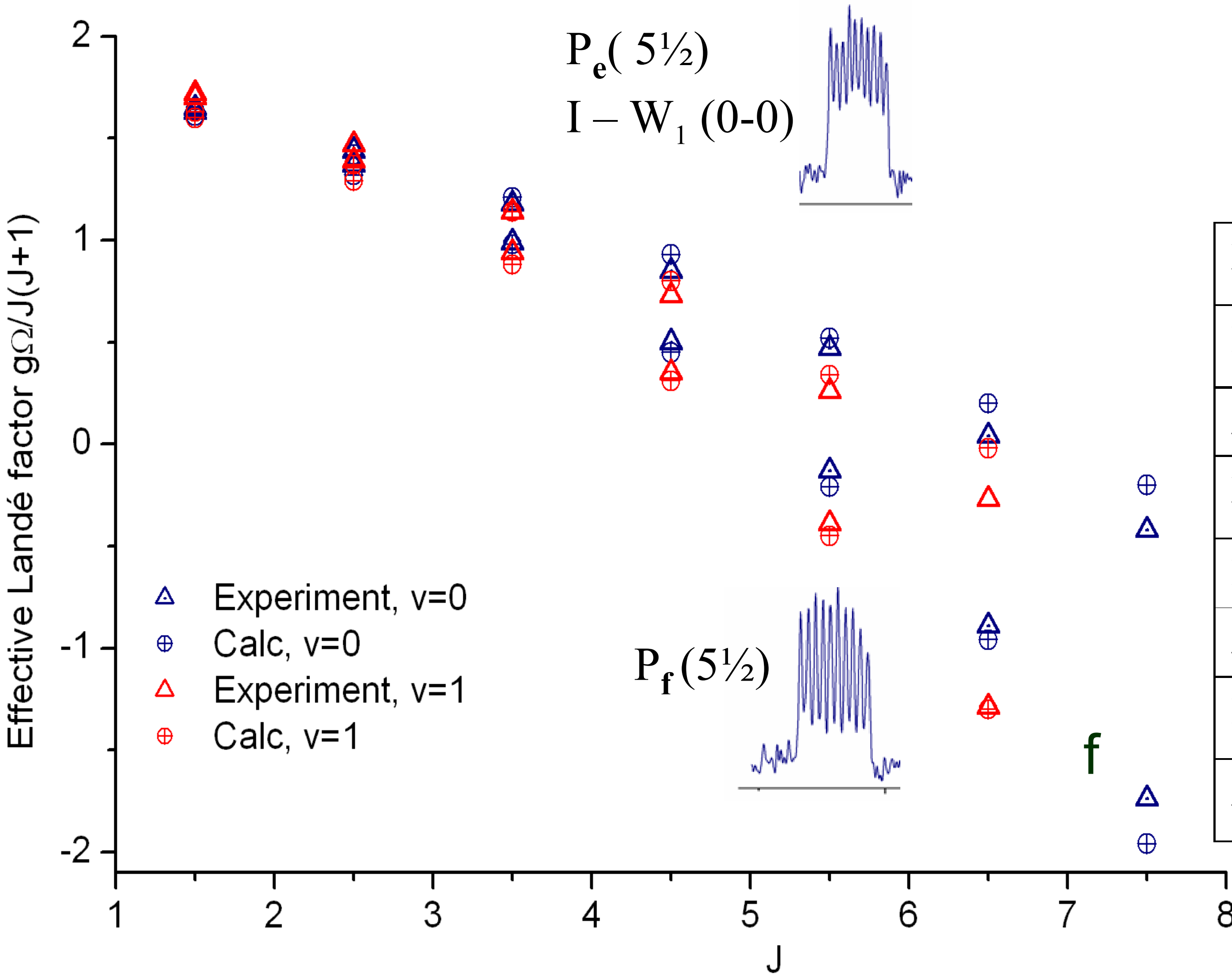
Collisionally induced fluorescence has allowed us to access a single vibrational level of a previously unobserved electronic state of NiH.

We assign it as v=0 of 2 $^2\Pi_{1/2}$

Transitions from this state have been recorded for ^{58}NiH and ^{60}NiH. These greatly enhance the observations we have for the low-lying 1 $^2\Pi_{1/2}$ state, whose levels are systematically more than ~30 % $^2\Sigma^+$ in character.

We are grateful to the CNRS and to the French funding agency ANR for financial support (ANR-08-BLAN-0017) received for this project.

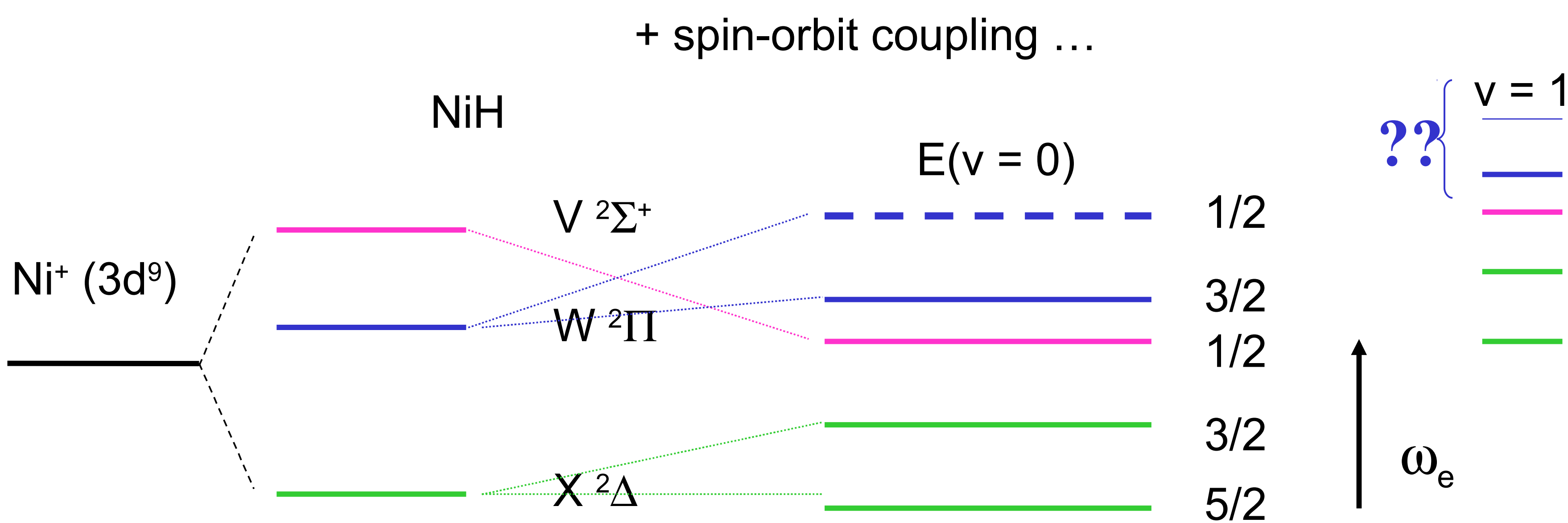
Satisfactory outcome … Example, W_1, $^2\Pi_{3/2}$



% Composition

Parity	e (Δ)	f (Δ)	e (Δ)
Σ v=0		2	
$\Pi_{3/2}$ v=0	69	67	
$\Delta_{3/2}$ v=0	6	6	
Σ v=1			1
$\Pi_{3/2}$ v=1	0	2	79
$\Delta_{3/2}$ v=1	20	20	8
$\Pi_{3/2}$ v=2			2
$\Delta_{3/2}$ v=2			8

More observations required to describe the 3d complex of low-lying states (X $^2\Delta$, W $^2\Pi$, V $^2\Sigma^+$) in NiH : plenty of information for Ω = 5/2 and 3/2



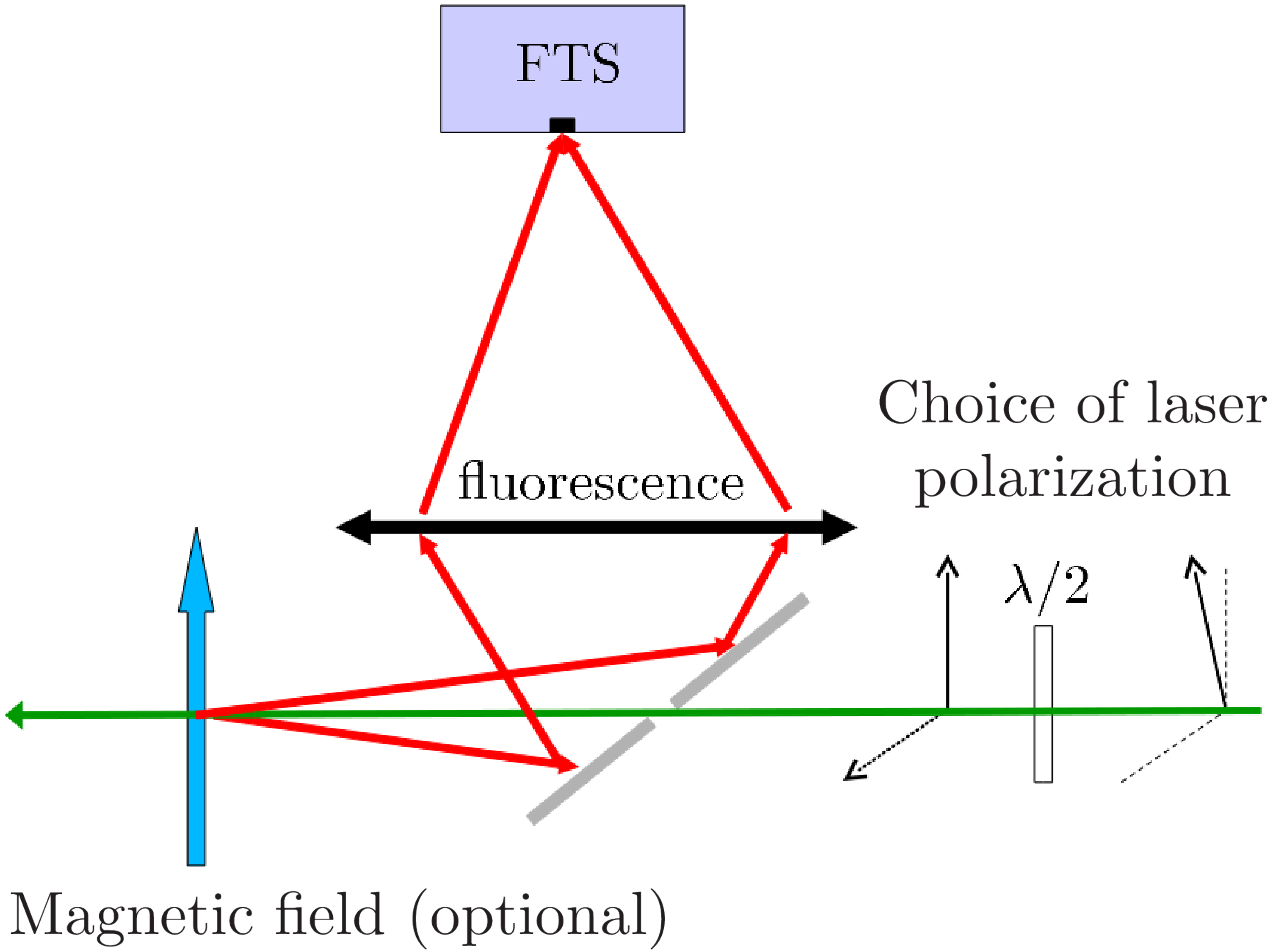
'**Supermultiplet**' model Gray, Li, Nelis and Field, J Chem. Phys 95 7164 (1991)

Retrieve X $^2\Delta$, W $^2\Pi$, V $^2\Sigma^+$. energies with a « modest » set of Dunham parameters Y_{ij} (i,j ≤ 2), a single spin-orbit parameter ζ_{3d}, L uncoupling, and integrals from RKR curves.

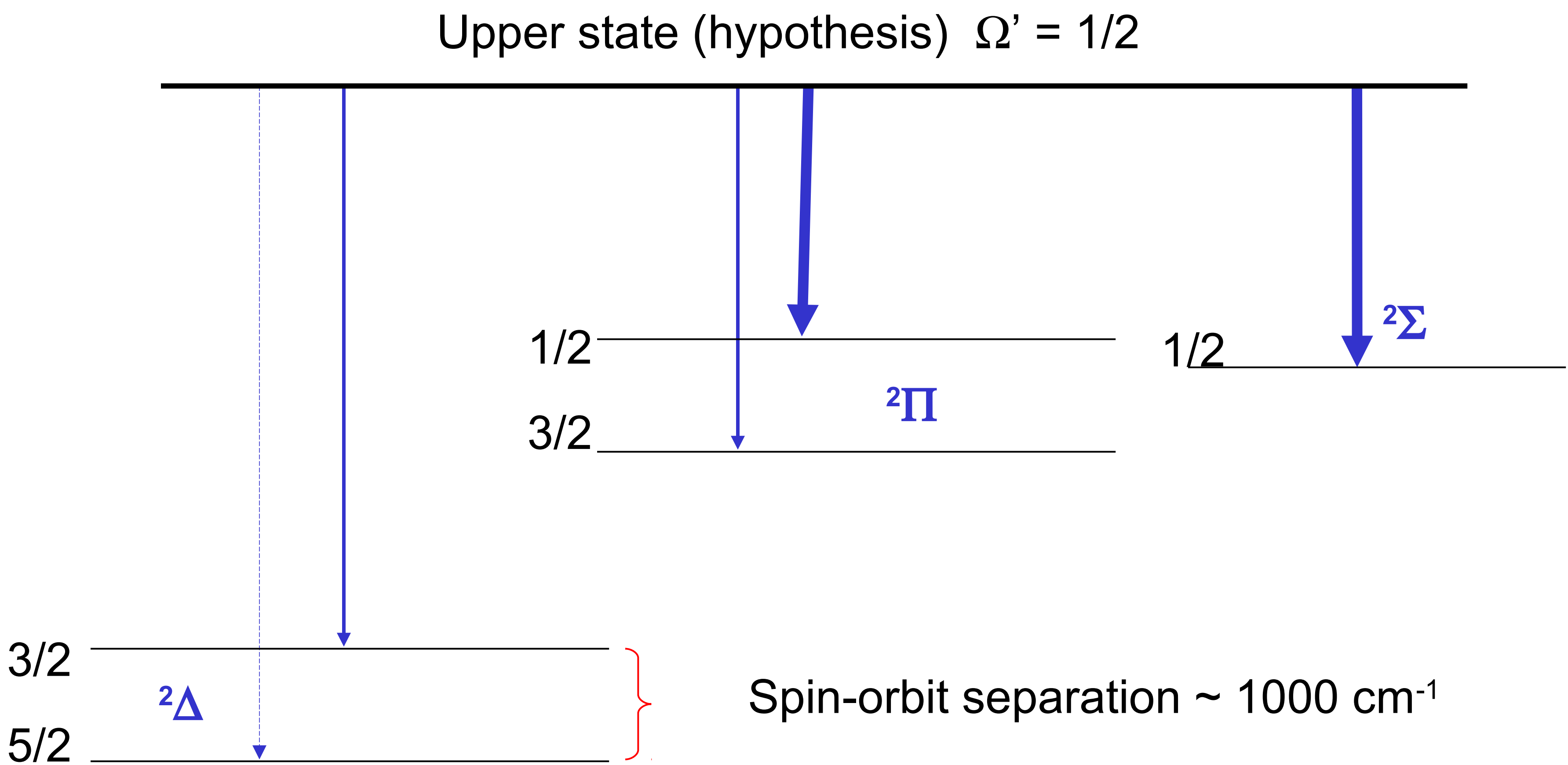
Predictions were given up to v=1.

Calc $_{(Gray)}$ – Obs $_{(now)}$ varies up to 4 cm^{-1} . σ_{exp} is now 0.005 cm^{-1}. Re-fit data.

FT Spectroscopy : isotopically selective



Assuming collisions populate a so-far unknown Ω’ = 1/2 state
we expect to observe transitions occur to Ω" = 1/2 and Ω " = 3/2 states.



ASSIGNMENT? Laser populated known level, J 3.5, e and f parity,
T' = 18474.01 cm^{-1} above J" = 2.5 $^2\Delta_{5/2}$.

NEW TRANSITION likely to have T’ ~18500 ± 1000 cm^{-1}, so T" ~ 4000 cm^{-1}
The most likely lower state would then be W_2 $^2\Pi_{1/2}$. But no obvious ‘comb-diffs’ to confirm.

Closer view of the same spectrum. More branches emerge.
But still with NO recognizable combination differences !

In magenta : unassigned lines.

In blue : assigned lines.