A Reinvestigation of the C_2 Deslandres-d'Azambuja Transition

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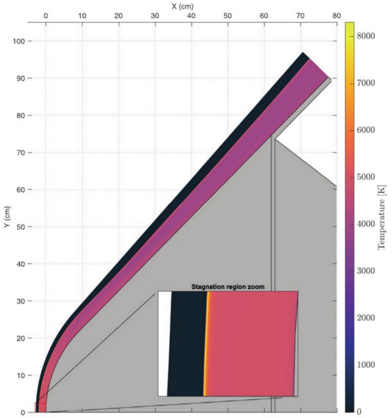
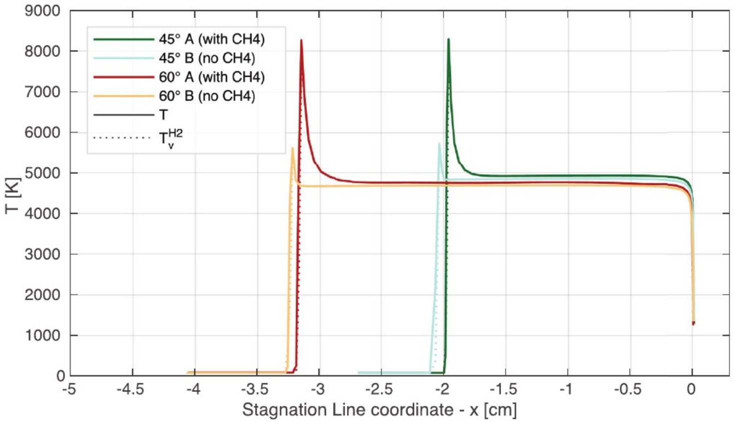
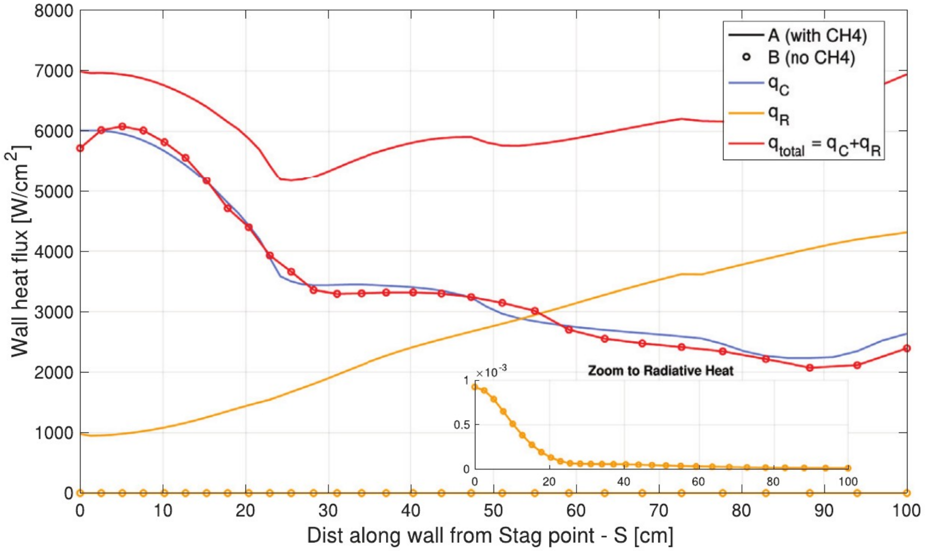
Scope

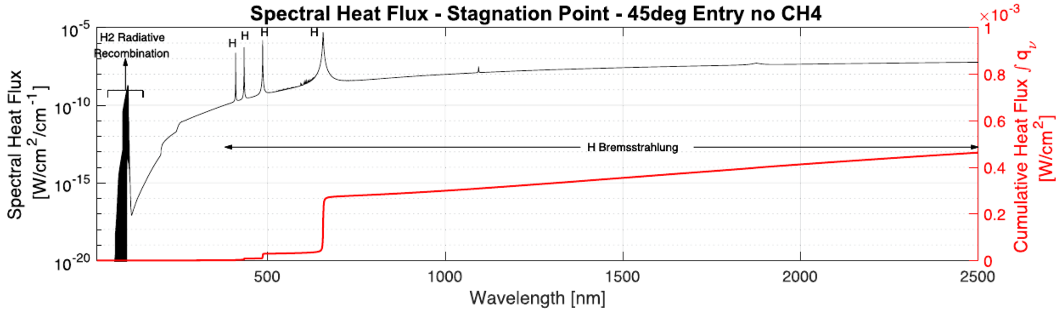
- Park (J. Spaceraft Rockets 2011, J. Thermophysics Heat Transf. 2012, J. Spaceraft Rockets 2014) postulated that minor concentrations of CH_4 in Neptune atmosphere would enhance radiative heating through radiation from atomic C and molecular CH
- Coelho (Adv. Space Res. 2023) performed updated CFRD calculations with Ray-Tracing techniques for radiative transfer, accounting for all possible radiative species (with additional accounting of C_2 radiation)
  - Coelho's predicted radiative heating same order of magnitude than convective heating, if the 1.5% CH4 in Neptune (NeptuneGRAM 2004) accounted for, even for lower entry speeds (~18km/s)
  - Previous simulations and testing, pre- and post-Galileo showed that pure H_2/He flows are essentially radiationless for velocities below 27km/s.

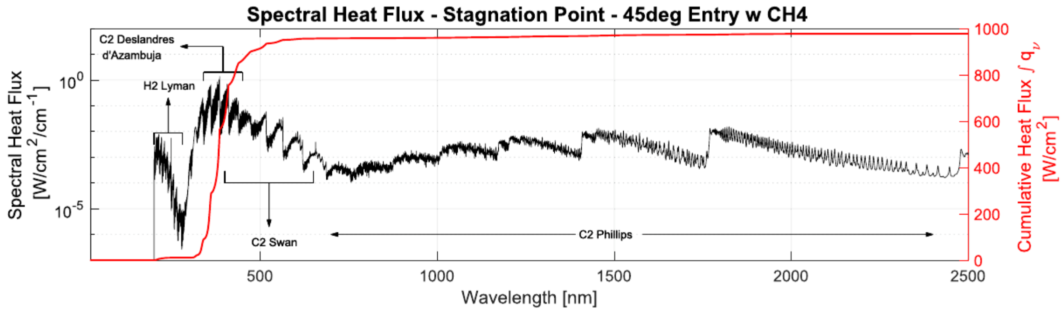




Ray-Tracing results for Radiative Heating
(Coelho 2023)







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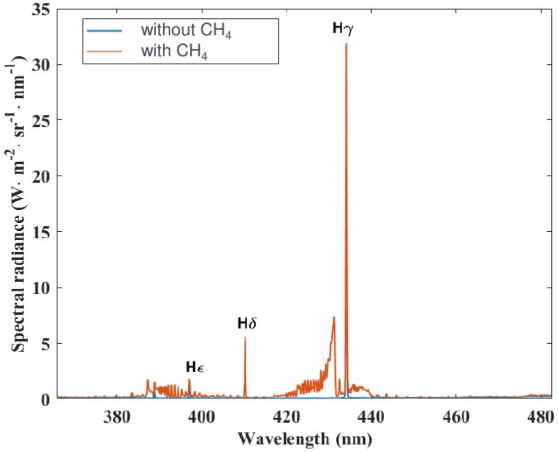
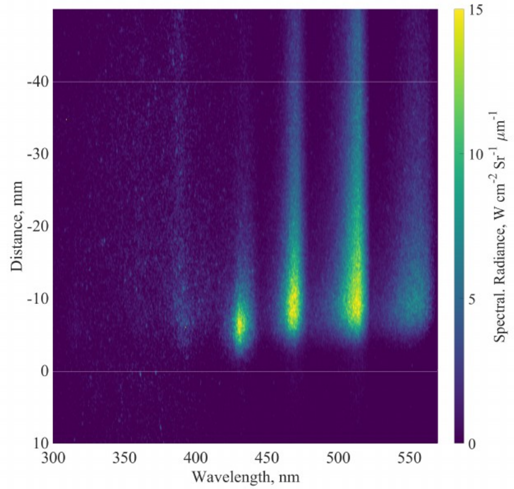
Scope (ctd.)

- TRP activity sponsored by ESA ensued (2023-2024), led by IRS, testing on Plasma wind-tunnels (PWK1, Stuttgart) and Shock-Tubes (T6, Oxford). In parallel, some shots with the addition of CH_4 to H_2/He flows carried out at EAST.
  - Significant radiation by CH and C_2 species observed experimentally, after being predicted theoretically/numerically.



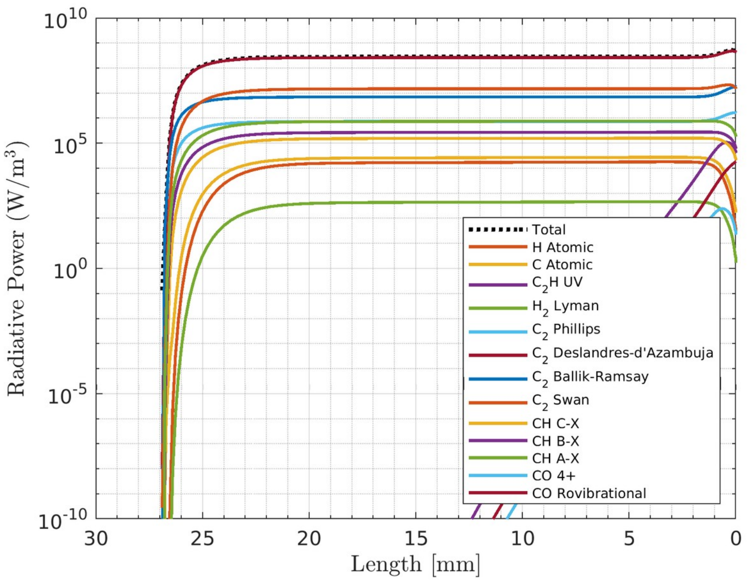
PWK1, IRS (left);
T6, Oxford (right)

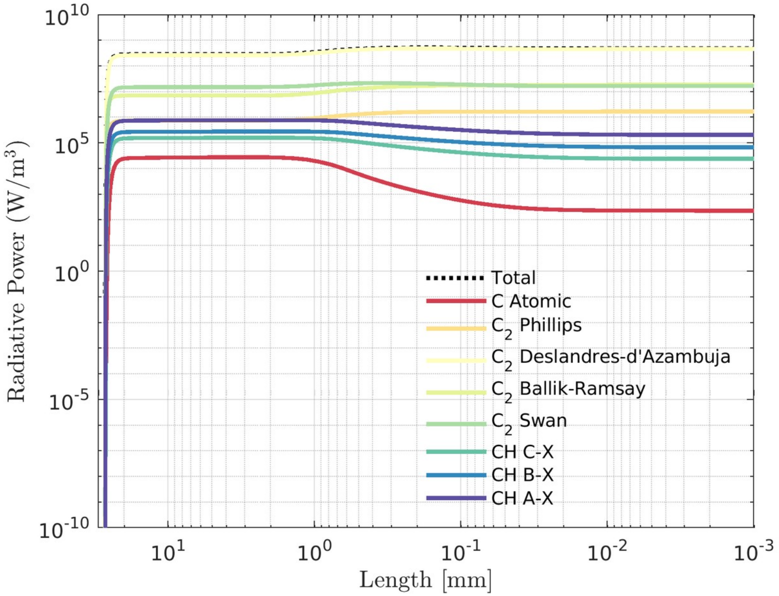


Scope (ctd.)

- Ice Giant Sensors activity includes numerical modeling
  - FGE provides CFD flowfields including ablation for Uranus and Neptune Entries
  - Space Ballistics providing radiative transfer calculations for a Galileo-type shape (discussed Thursday in another presentation)
- Simulation results confirmed previous Coelho results
  - Predominance of radiation from the C_2 Deslandres-d'Azambuja radiative system
  - C_2 Swan contributes as a far second

Contribution of C_2 Deslandres-d'Azambuja to Irradiance





- Neptune A0 point, high-pressure, thermal equilibrium, chemistry in quasi-steady-state
- The radiative species that mostly contribute to the total Irradiance are C2 Deslandres d'Azambuja and C2 Swan (more than an order of magnitude less

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The Question:

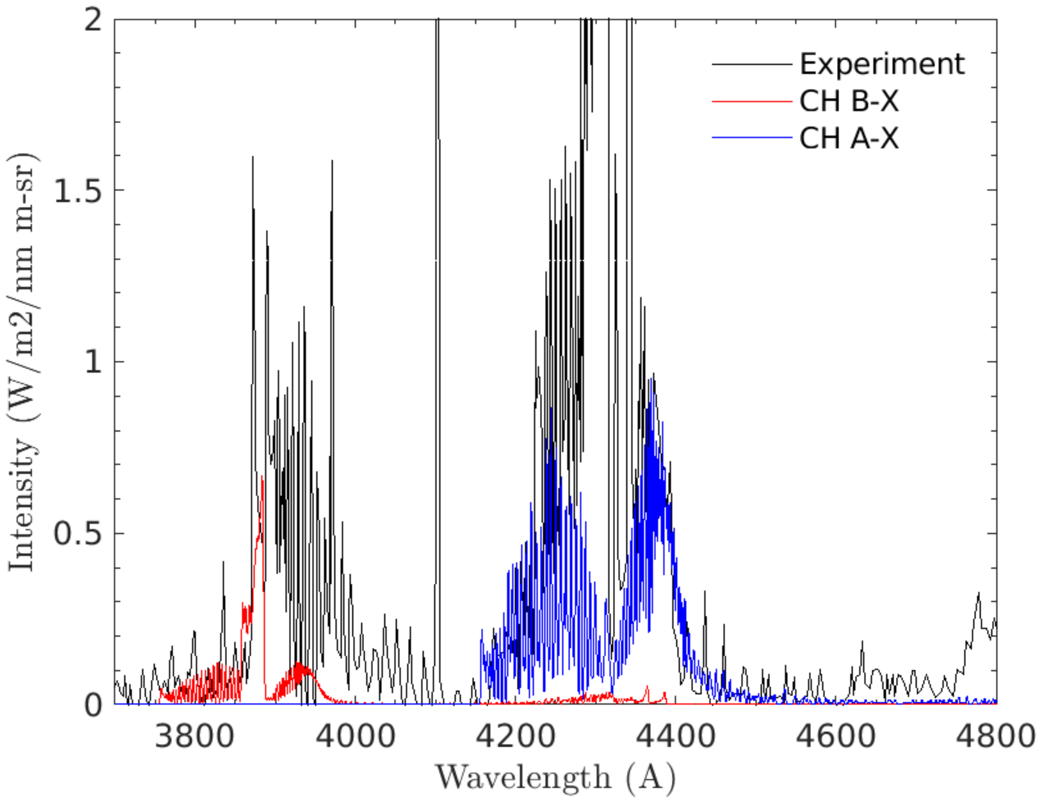
- The C2 Swan is quite ubiquitous in plasma applications, radiating in a multitude of carbon-containing plasmas (e.g. Lino da Silva 2004, Ph.D. Thesis)
- In comparison, the C_2 Deslandres-d'Azambuja radiative system is mostly absent
- So can the radiative database be trusted when it is predicting that C_2 Deslandres-d'Azambuja is a dominant radiative system?
- Plus, the C_2 Deslandres-d'Azambuja is a relatively obscure radiative system, lacking contemporary studies
  - "*A high resolution study of the Deslandres–d'Azambuja bands for $^{12}C_2$ is overdue.*" (McKemmish et al, 2020, An update to the MARVEL data set and ExoMol line list for $^{12}C_2$)

...Lets numerically rebuild the available experimental data.

Available data

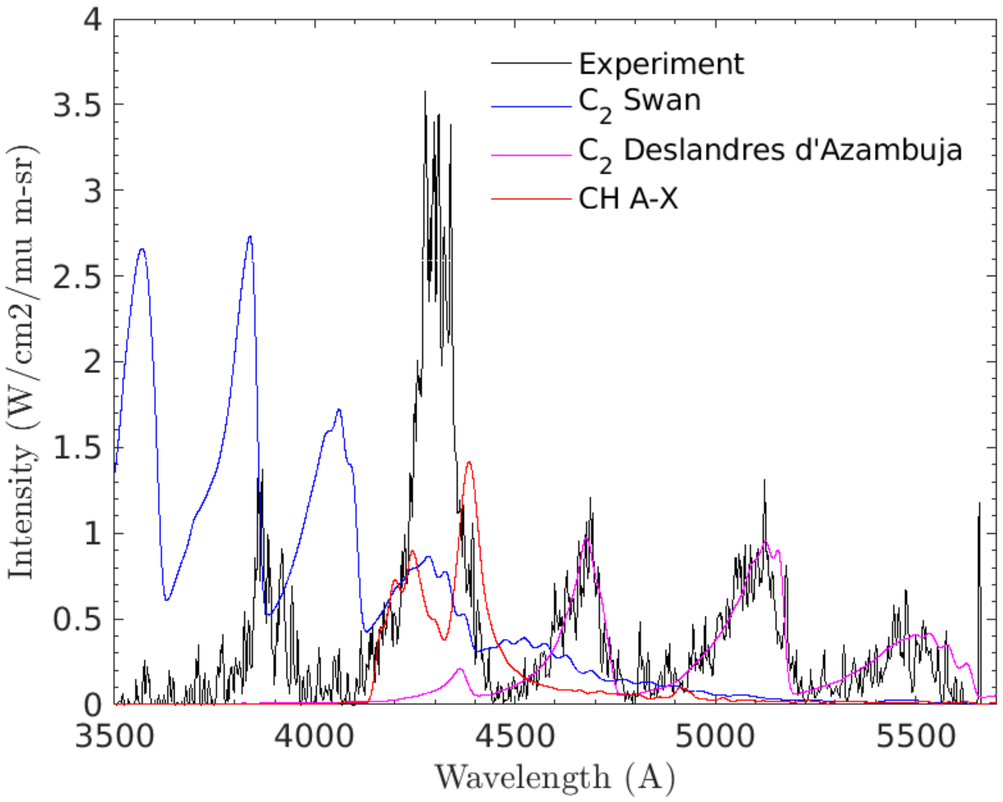
- PWK1 plasma wind-tunnel data
- EAST Shock-Tube Test suite 67 data
- T6 A, B, C test points
- Absorption Spectra from White Dwarf Stars

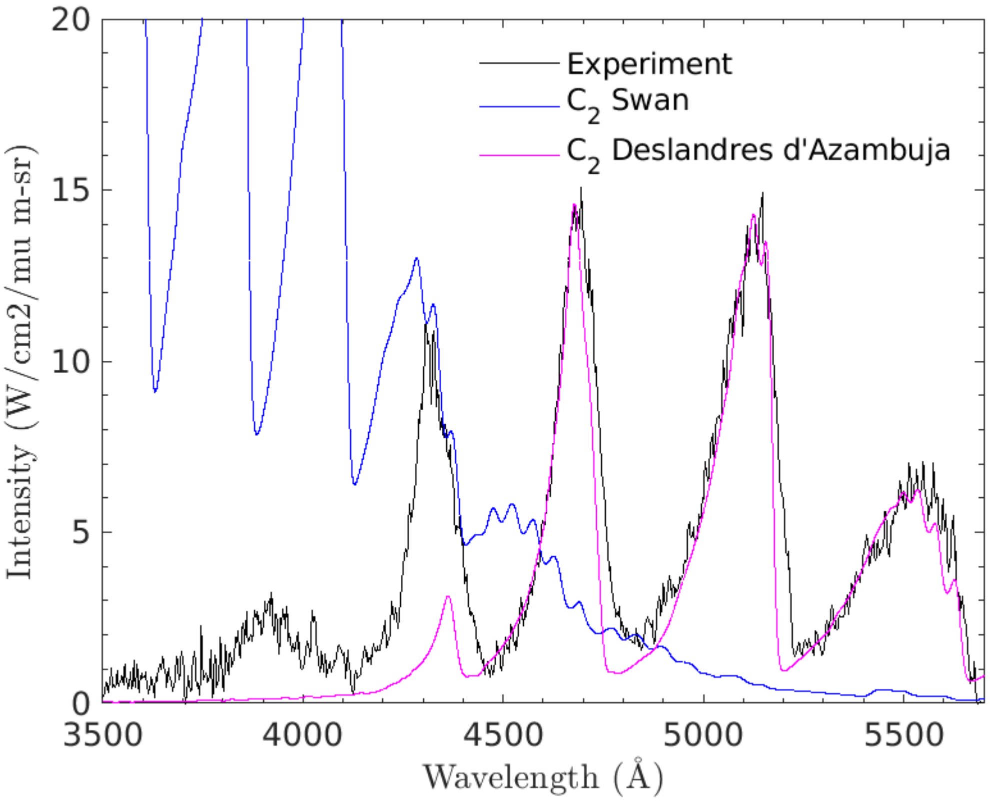
PWK1 Test



Experiment
CH B-X
CH A-X
Intensity (W/m2/nm m-sr)
Wavelength (A)
0
0.5
1
1.5
2
3800
4000
4200
4400
4600
4800

T6 Tests B and C





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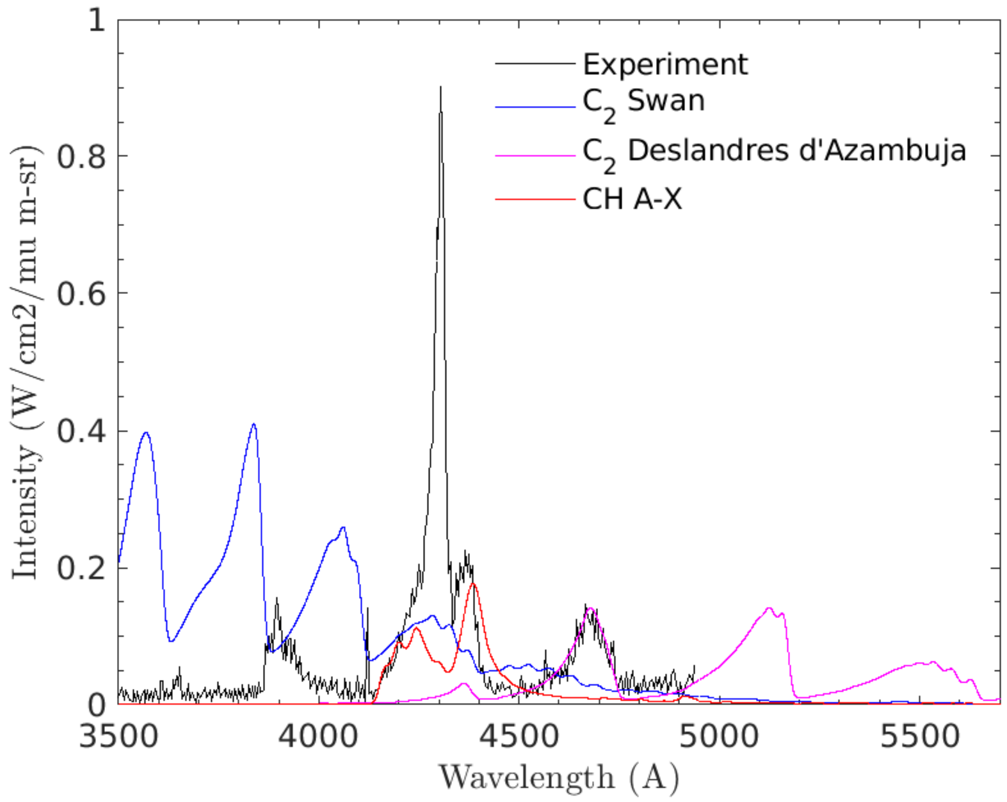
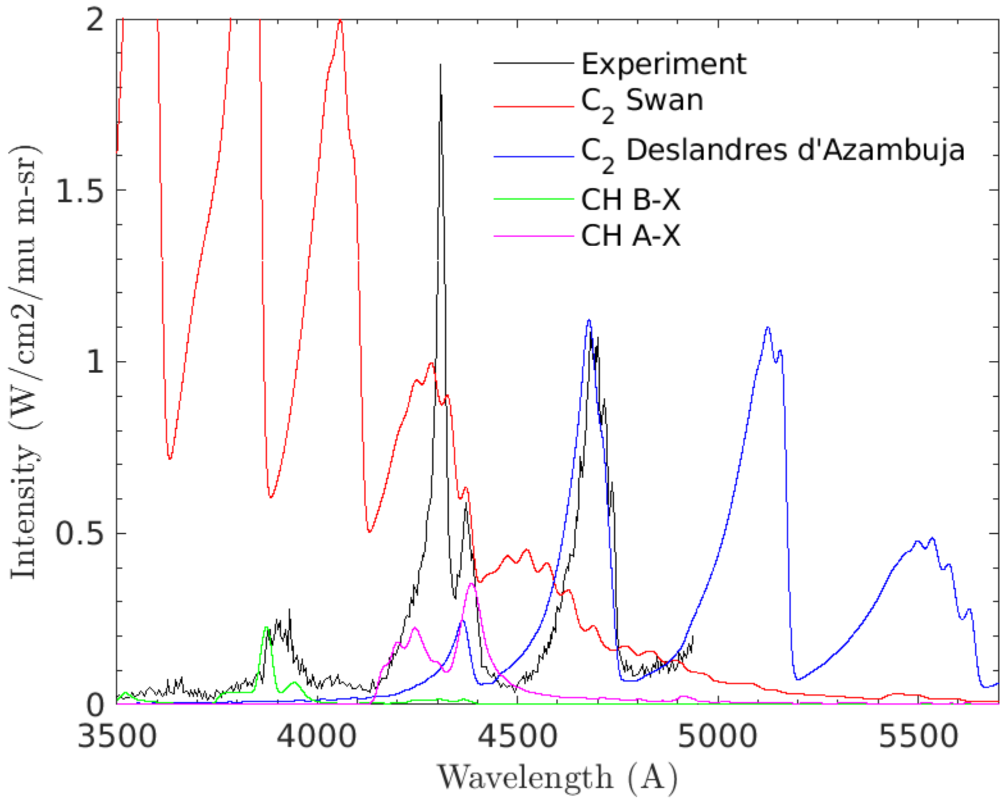
EAST Tests 67-9 and 67-16





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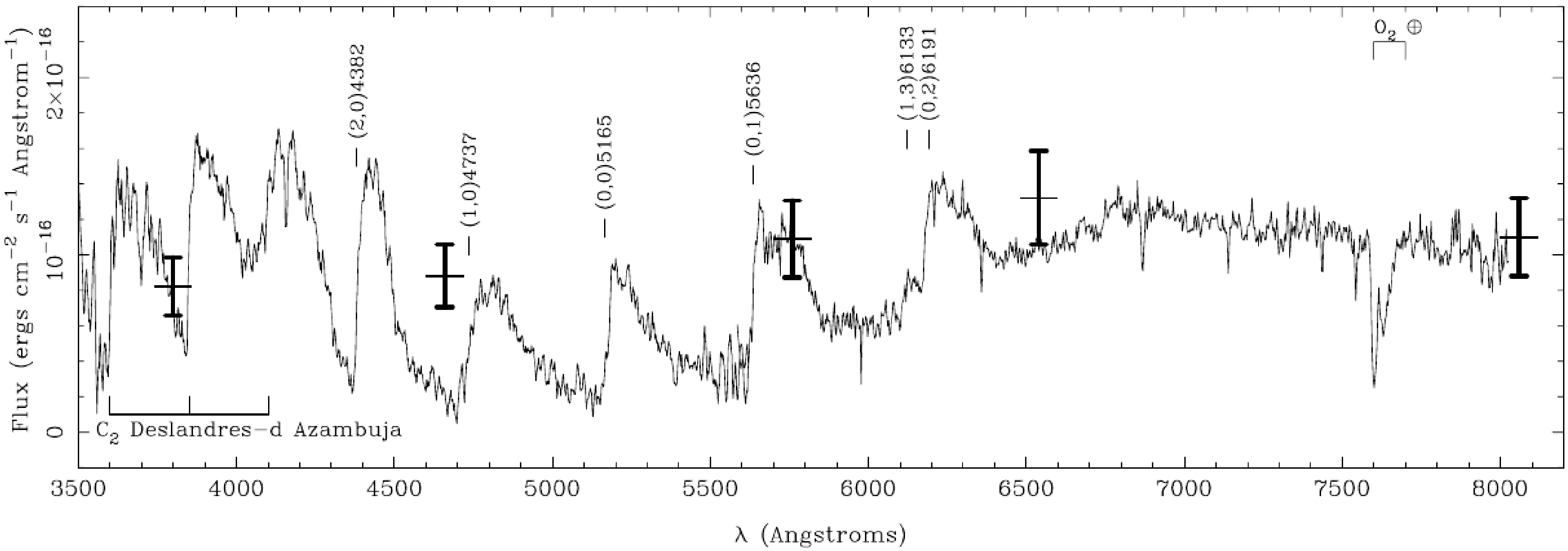
Carbon-Rich White Dwarf Star Spectra



- Very interesting spectrum (absorption of Blackbody radiation at T=5000K by the star photosphere allows identifying the C2 Deslandres d'Azambuja system, not yet simulated due to lack of time.

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Simulation Results

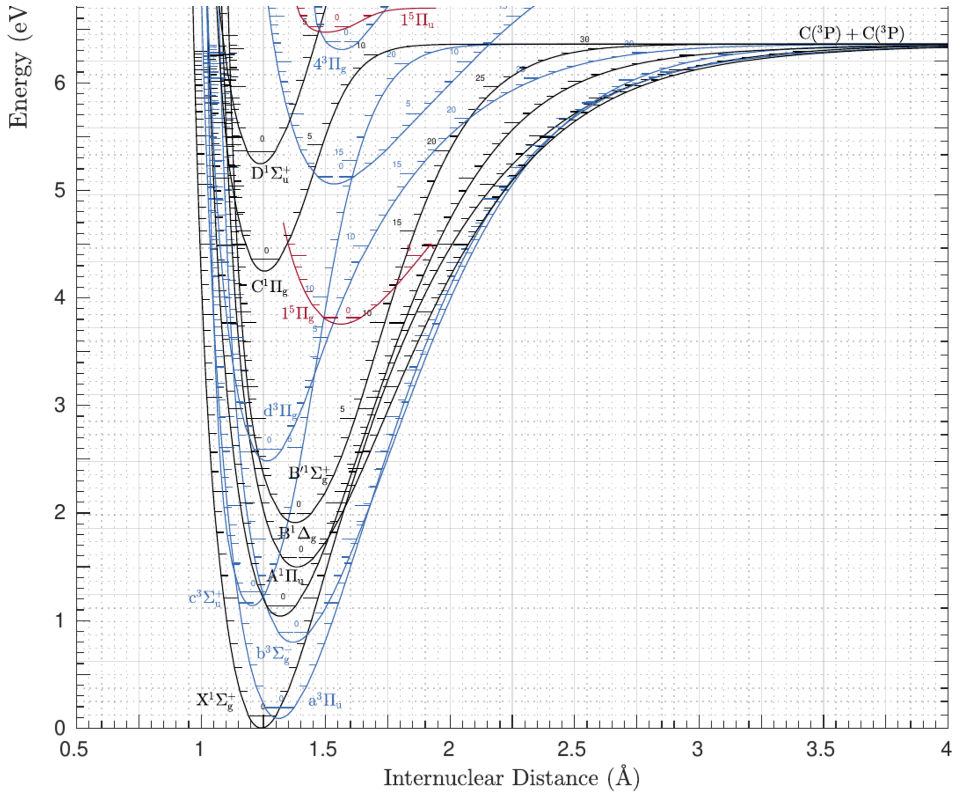
- C_2 Swan bands always absent
- CH A-X and B-X prominent on PWK1, observable on low-CH_4 concentration shots in EAST and T6
- C_2 Deslandres d'Azambuja bands prominent on all shock-tube tests

	PWK1	T6 B	T6 C	EAST 67-9	EAST 67-16
%CH4	1.5	0.5	5	0.4	0.4
p_inf (Pa)	N/A	12.8	13	13.3	66.5
v_inf (km/s)	N/A	16.4	16.3	16.3	19.24
Tr	5000	8500	8500	8500	8500
Tv	5000	9500	9500	9500	9500
n_C2	0	3.00E+17	4.50E+18	4.50E+16	3.50E+17
n_CH	5.00E+18	8.00E+17	5.00E+18	1.00E+17	2.00E+17

Reinvestigating the radiative database

A look at the Potential curves of C2

- C2(C) and C2(d) formed by recombination
  - C+C+M → C2+M
  - C+C → C2+hν
- C2(C) is higher so it should be more easily populated (the less ΔE the better...)

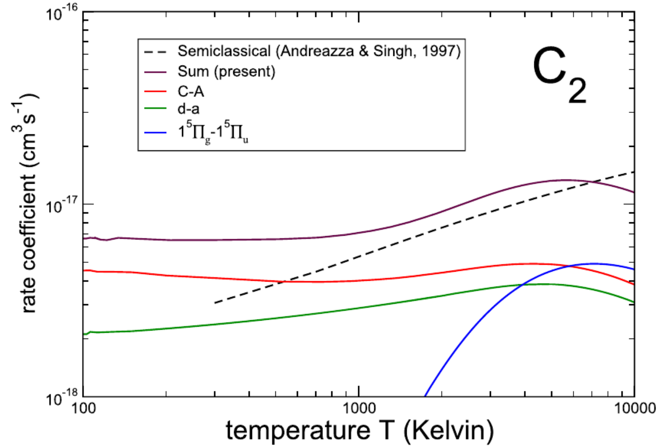


Old and New theoretical studies

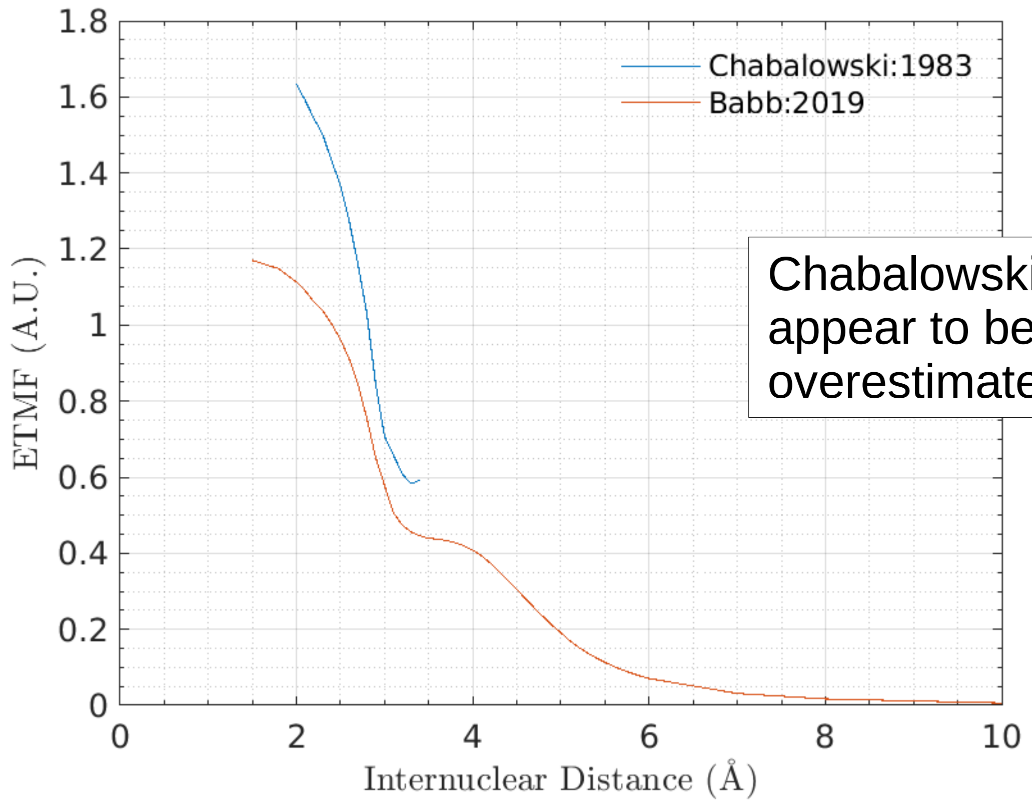
- Einstein coefficients for the C_2 Deslandres d'Azambuja system based on Chabalowski:1983 ETMF, which verified his results against limited shock-tube experiments from Cooper:1979
  - His results slightly overestimated the data from cooper
- Babb, Astropys. J. Studied theoretically the radiative recombination of C_2
  - C+C→C2+hν
- Proposes rates of population for the two systems…
- ...and has contemporary calculations for a new ETMF for the C_2 Deslandres d'Azambuja system

Table 3
Comparisons between theoretical and experimental transition properties

Transition	ν_{00} (eV)	ΔE_e(eV) [a]	f_{00}
$b^3\Sigma_g^- - a^3\Pi_u$	0 703	0 737	0 00123
Ballik–Ramsay	(0 698) [b]	0 683	(0 00118) [c]
		(0 798)	
$D^1\Sigma_u^+ - X^1\Sigma_g^+$	5 502	5 511	0 0544
Mulliken	(5.359)	5 504	(0 055 ± 0 006) [d]
		(5 361)	(0 0171) [c]
$C^1\Pi_g - A^1\Pi_u$	3 391	3 325	0 0401
Deslandres–	(3 220)	3.388	(0 0267) [c]
d'Azambuja		(3 207)	
$A^1\Pi_u - X^1\Sigma_g^+$	1 009	1 009	0 0027
Phillips	(1 025)	1 026	(0 0025 ± 0 0002) [e]
		(1 040)	(0 00394) [c]
			(0 0023 ± 0 0003) [f]
			(0 0015) [f]
			(0 00141) [g]



Transition Moments Comparison



Chabalowski ETMF does appear to be slightly overestimated

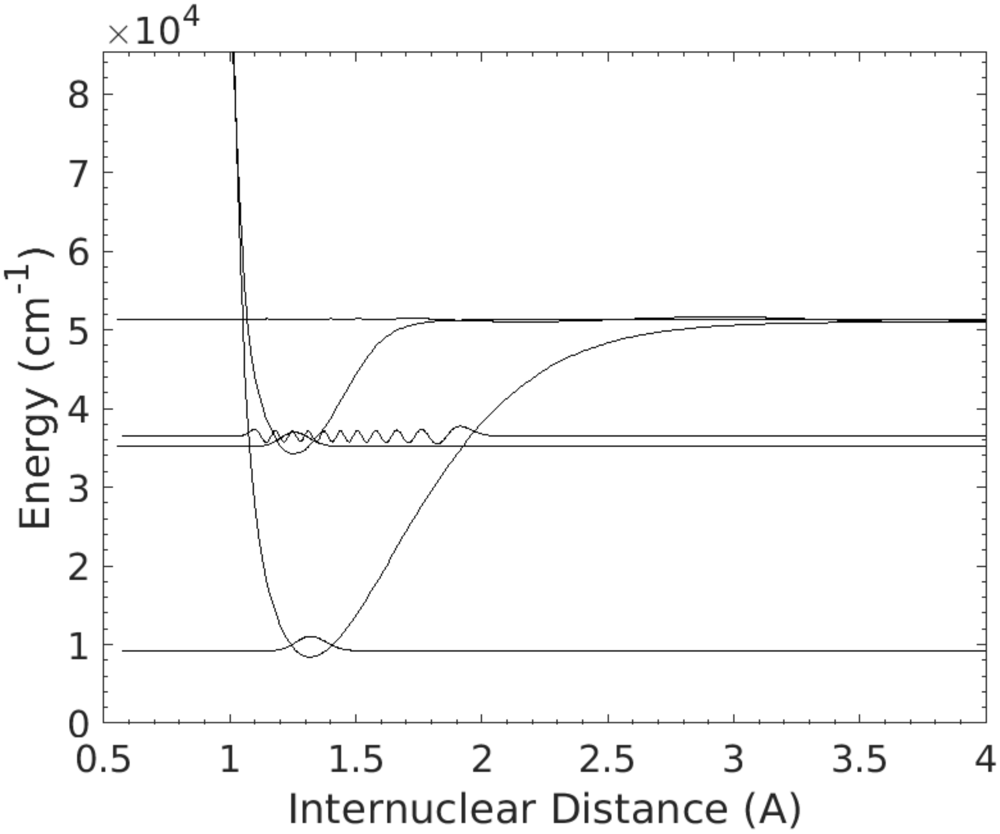
New Einstein Coefficients

- Used the new ETMF and reconstructed potential curves wavefunctions to get newer Av’v” coeffs.

- $$R_e^{v'v''} = \int \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr$$

- $$A_{v'v''} = \frac{64\pi^4 \overline{\nu}^3 (2 - \delta_{0,\Lambda'+\Lambda''})}{3hc^3 (2 - \delta_{0,\Lambda'})} \left(R_e^{v'v''} \right)^2$$

- Numerical calculations from the RKR_SCH routine of the SPARK Line-by-Line code



Chabalowski vs. New Einstein coeffs.

Table 7

Spontaneous emission probabilities $A_{v'v''}$ (in s^{-1}) for the Deslandres–d'Azambuja band system

v'	v''							
	0	1	2	3	4	5	6	7
0	2 00+7	1 06+7	4 18+6	1 38+6	4 08−5	1 11−5	2 75+4	6 34+3
1	1 73+7	3.27+6	6 90+6	4 98+6	2 31−6	8 74+5	2 89−5	8 53+4
2	2 18+6	1.92+7	4 93+5	3 49+6	4 24+6	2 52−6	1 14−6	4 32+5
3	5 43+4	2 54+6	1 88+7	2 45+5	1 64+6	3 33+6	2 25−6	1 20−6
4	3 21+4	5.40+5	1 08+6	1 71+7	6 39+5	6 82+5	2 84+6	1 68+6
5	9.18+3	1 47+4	1 69+6	4 80+4	1 22+7	1 77+6	1 44+5	2 93+6
6	3 47+2	4 60+4	1.25+5	1 68+6	3 14+6	4 04−6	2 48+6	3.77−3
$\tau(v')$ (ns)	27	28	33	33				

1.711E+7	8.536E+6	2.612E+6	6.400E+5	1.385E+5	2.777E+4	5.343E+3	1.034E+3	2.141E+2	5.106E+1	1.453E+1
1.242E+7	2.599E+6	7.423E+6	4.413E+6	1.631E+6	4.781E+5	1.228E+5	2.948E+4	6.984E+3	1.730E+3	4.727E+2
3.229E+6	1.328E+7	2.416E+4	3.946E+6	4.641E+6	2.499E+6	9.615E+5	3.088E+5	9.018E+4	2.556E+4	7.431E+3
3.542E+5	6.784E+6	9.732E+6	1.699E+6	1.219E+6	3.688E+6	2.903E+6	1.444E+6	5.705E+5	1.994E+5	6.633E+4
1.246E+4	1.078E+6	9.369E+6	5.636E+6	3.802E+6	6.626E+4	2.275E+6	2.760E+6	1.766E+6	8.477E+5	3.507E+5
3.070E-1	4.261E+4	1.997E+6	1.070E+7	2.698E+6	4.826E+6	1.992E+5	1.024E+6	2.191E+6	1.821E+6	1.052E+6
3.306E+1	2.804E+2	6.633E+4	2.778E+6	1.112E+7	1.226E+6	4.656E+6	8.738E+5	2.873E+5	1.469E+6	1.614E+6
2.252E+0	4.798E+2	6.121E+3	3.273E+4	2.962E+6	1.122E+7	7.930E+5	3.823E+6	1.453E+6	3.072E+4	8.684E+5
4.845E-1	1.207E+1	2.353E+3	4.035E+4	8.746E+3	2.223E+6	1.129E+7	1.121E+6	2.700E+6	1.722E+6	1.296E+2
5.062E-1	3.323E+0	1.107E+2	1.251E+3	9.645E+4	3.235E+5	6.517E+5	1.025E+7	2.574E+6	1.378E+6	1.815E+6
3.538E-4	4.425E+0	5.334E+1	2.315E+3	7.740E+3	3.874E+4	1.030E+6	2.404E+5	5.318E+6	4.812E+6	2.287E+5

Conclusions

- There is now better confidence on the importance of the C_2 Deslandres d'Azambuja and the correctness of the radiative database (authors opinion)
- The reasons why we sometimes observe emission from the C2 Swan system and other times from the C_2 Deslandres d'Azambuja system remain mysterious
  - Great topic of study for plasma chemistry/state-to-state/collisional radiative modelling
  - C_2 Deslandres d'Azambuja is also the dominant system in equilibrium, high-pressure conditions